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INVESTIGATION OF REACTIVITY OF LAUNCH VEHICLE MATERIALS WITH LIQUID OXYGEN

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ABSTRACT

This is the second annual report of a study of the causes of the impact sensitivity of various organic materials with liquid oxygen. The overall aim has been to examine the hypothesis that free radical formation and reactivity are the primary cause of impact ignition.

For the first phase we have chosen to study the mechanism of formation of radicals by impact and related processes and, further, to establish what conditions might be required for ignition of radical-laden samples. Earlier studies had confirmed that grinding of polystyrene produced large quantities of carbon radicals. During this report period we have established the similarity between these radicals and impact-produced radicals. Further, we now know that these radicals react rapidly and spontaneously with oxygen to produce peroxy radicals. However, the reaction is not sufficiently exothermic nor the products sufficiently unstable for the reaction to propagate through the substrate. Thus we have sought and found evidence that hot spot formation, as proposed by Bowden in a different context, is required. This evidence has been acquired from photographs of impacted samples which show that ignition originates at one or more points and from experiments in which the inclusion of an abrasive can increase the apparent sensitivity of a low melting sample. We are now devising experimental methods to obtain high speed motion pictures of a sample being impacted and to heat polymer-LOX mixtures abruptly. From the photographs we expect to learn more about deflagration propagation and from the heating studies we expect to relate decomposition kinetics to impact sensitivity.

The second phase of the study is concerned with the reactions of carbon and peroxy free radicals at low temperatures. During the first annual report period we studied the photolyses of azoisobutane and azoisopropane in the presence of oxygen at 140-180°K. An unstable polyoxide was detected from interactions of t-butyl peroxy radical but not from interaction of isopropyl peroxy radicals. During this second year we have continued our study of t-butyl peroxy radical reactions using improved techniques for carrying out and analyzing such reactions. Careful studies of the photolyses of t-butyl iodide-oxygen and trifluoromethyl iodide-oxygen systems have been done in a similar way. A structure proof for the azoisobutane photoproduct was completed. Chemical and physical characterization of samples of fluorosilicone grease are also reported.

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I INTRODUCTION

Many materials in contact with liquid oxygen (LOX) are explosion hazards when subjected to impact, heat, or other forms of energy. Selection of materials for safe use in a LOX environment is based on an arbitrary test which subjects materials to impact under LOX.[1] Rocket construction materials selected by this empirical method have been satisfactory, but it is possible that some materials that could be adequate have been eliminated. Improved selection methods are needed, but design of such methods is dependent upon a more complete knowledge of the conditions and mechanisms necessary for ignition in the presence of LOX. It is the purpose of this study to examine and identify these conditions and mechanisms.

Explosions or rapid oxidations resulting from impacting organic compounds in the presence of LOX very likely involve formation of carbon radicals at some step. Neither the way in which these radicals are initially produced nor the way in which they are converted to final products in exothermic reactions with oxygen is well understood. Such knowledge seems essential for predicting or altering the behavior of impact-sensitive systems.

Oxidation of organic compounds at elevated temperatures is usually a complicated free radical chain reaction involving initiation from some free radical source, propagation, and termination. The important features of these reactions involving hydrocarbons are fairly well known.[2] Because free radicals are important in ignition at elevated temperatures, we suspect that they play an equally important role at low temperatures.

This is the second annual report of a NASA-supported study of the causes of impact sensitivity of various organic materials with liquid oxygen. The experimental program has been conducted in two phases.[3] In the first phase we established that polystyryl free radicals are produced in relatively large quantities by impact and by grinding. However,

these radicals do not propagate at low temperatures. We are now investigating the conditions that will cause ignition of organic materials containing these radicals. The second phase began with photolytic generation of radicals and is continuing with a detailed study of the reactivity of t-butyl, isopropyl and trifluoromethyl radicals with gaseous oxygen at low temperatures under a variety of environmental conditions. Polyoxide intermediates are formed from t-butyl radicals. The results of both phases of the program should help elucidate the mechanism of impact ignition and the relationship between structure and reactivity, thus permitting improved design or selection of safer materials.

II TRIBOCHEMICAL REACTIONS

A. Background

Impact testing provides practically no information on the mechanism of LOX-hydrocarbon reactions. Insufficient energy is supplied by the impact to raise the entire sample to ignition temperature, and it has been the purpose of this phase of the research to examine how the available mechanical energy is converted to chemical energy and how, once initiated, the impact-produced reactions propagate.

Last year we established that the grinding of polystyrene, a typical hydrocarbon polymer, produced large quantities of surface free radicals which were relatively stable at cryogenic temperatures. This year we have been able to show that similar types and quantities of radicals are produced by impact. It has, however, proven surprisingly difficult to ignite fine polystyrene powders even when they contain free radicals. Admission of oxygen to radical-laden particles may lead to a chemiluminescent reaction and generally converts carbon to oxyradicals of similar concentration. The surface radicals are, however, quite stable and persist for several minutes even at room temperature. Therefore, there must be another requirement for impact ignition and, following Bowden's lead,[4] we are now investigating whether hot spots are intimately involved in the initiation process. Our present activities include both photographic and kinetic studies. We have obtained photographs of the impact process which strongly suggest that ignition, when it occurs, does so at a few isolated sites from which combustion propagates. We are currently modifying our methods so that high speed photographs can be taken. To study the kinetic requirements we are exploring two different methods for abruptly heating polymer-LOX systems. The goal is to relate the sample temperature required for ignition to conditions which might prevail during impact testing. We have also performed some experiments which relate polymer physical properties to sensitivity. Because of the manner in which these experiments were done, the results lend additional support

to the hot spot theory. Details and additional discussion of our tribochemical research are in the sections which follow.

B. Free Radical Studies

1. Impact-Produced Radicals

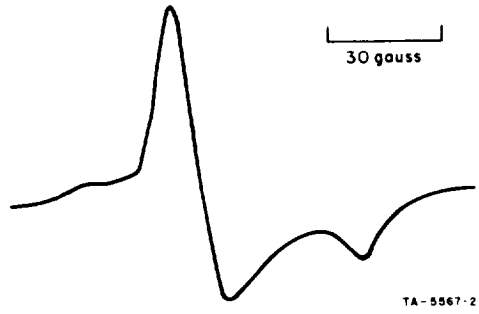
Since grinding and milling of polystyrene at very low temperatures readily produced large quantities of carbon radicals, much of our subsequent work has used samples produced this way. However, we endeavored to show that impact--as with the ABMA tester--produced essentially equivalent species. Accordingly, several samples of polystyrene were impacted under nitrogen coolant from 43.3 inches drop height on the ABMA tester. The impact produced a variety of small particles. Those which passed through an LN-chilled 30-mesh screen were collected for analyses by esr. To prevent contamination with water and oxygen from the air, the tester and transfer equipment were surrounded with plastic bags. Quartz esr sample tubes were filled with particles under a nitrogen atmosphere and the tubes were sealed after evacuation (10^{-4} torr) to remove any adsorbed oxygen which would complicate the esr spectra.

Results of two measurements of the esr spectrum of these particles indicate that 10^{13} to 10^{14} free radicals/gram were present on the samples. Figures 1a and 1b show spectra of typical samples produced by in vacuo grinding at 77°K; these usually contain 10^{16} free radicals/gram. Figure 1c shows a trace of the esr spectrum with a standard pitch sample trace for comparison.

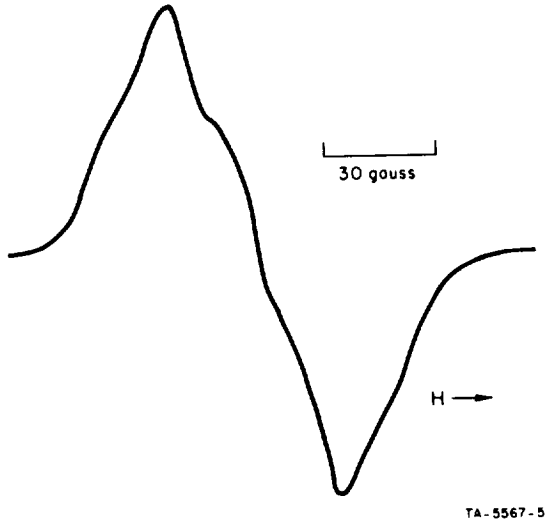
From the similarity of the spectra we conclude that grinding and impacting are almost equivalent operations in terms of their radical forming capabilities. Thus, the results acquired with samples obtained from grinding also apply to impact produced specimens.

2. Reaction of Oxygen with Ground Polystyrene

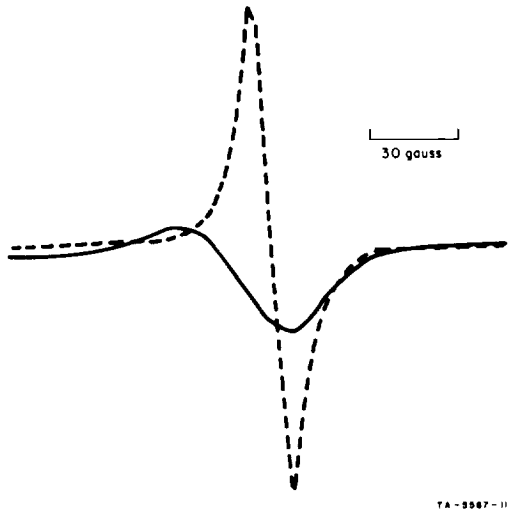
If impact ignition results only from the interaction of the mechanically produced radicals with cold oxygen, then treatment of powdered radical-laden polystyrene with cold oxygen should result in combustion.



(a) Containing peroxides



(b) Absence of oxygen



(c) —— SPECTRUM OF PARTICLES FROM ABMA TESTER
---- SPECTRUM OF STANDARD PITCH SAMPLE

FIG. 1 ESR SPECTRA OF DEGRADED POLYSTYRENE

From a variety of experiments we concluded, and previously reported, that spontaneous combustion is not a necessary sequel to the admixture of these two materials, even though we were able to show by esr that reaction occurs readily. Accordingly, though radicals may be necessary their presence is insufficient to cause ignition. Nevertheless, to elucidate further the structure of the radicals and their reaction with oxygen we did pursue one incidental observation of these experiments.

We attempted unsuccessfully to obtain a spectrum of the low intensity blue light produced when samples of free radical-laden polystyrene powders were treated with low pressure (50 torr) oxygen. The apparatus, shown schematically in Fig. 2, was not sufficiently sensitive when the entire visible region, or only a part of it, was scanned. However, we were able to obtain a color photograph of the reaction by wrapping Ektachrome Type B High Speed film around the sample tube and leaving it in place during an experiment. From this record and from visual spectrometric observations by a dark-adapted observer we concluded that the visible flash consisted only of blue light. As we will explain later, this is consistent with the esr evidence that radicals are involved in the low temperature oxidation process.

3. Role of Free Radical Inhibitors

The facile production of free radicals on polymers by grinding at 77°K suggests that the role of free radical inhibitors (antioxidants) be investigated in impact testing. When inhibitors are ground with polymers at about 80°K, the concentration of trapped free radicals is similar to that in pure polymers[5] because the high viscosity of the polymer prevents migration and reaction of the radical with the inhibitor. If the inhibitor is to be effective, it should be more intimately mixed with the polymer, as in solid solution. It is attractive to believe that the energy of impact may provide a hot spot and fluid state to allow the inhibitor to be effective and we sought to examine this hypothesis.

Incorporation of free radical inhibitors in polystyrene suitable for impact testing required considerable study before a method was found. Inhibitors such as Shell Chemical Company Ionol CP, m.p. 616°K, were too

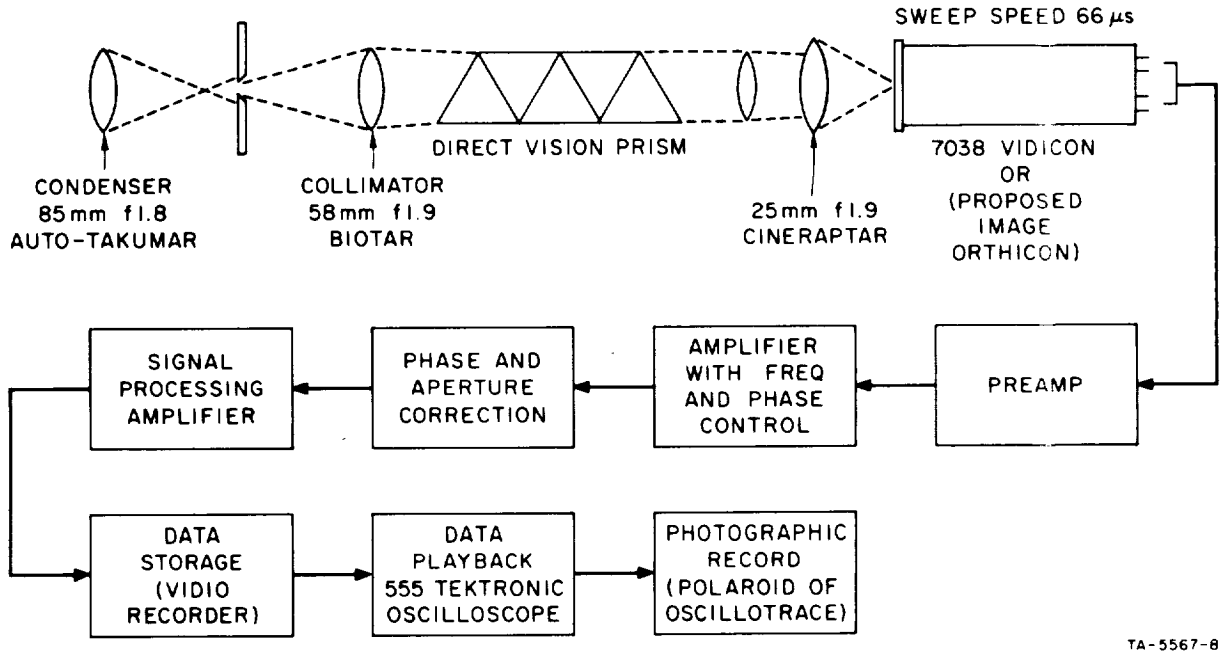


FIG. 2 RAPID SCANNING TAPE-RECORDING SPECTROGRAPH SYSTEM

volatile to be heated in vacuo to 473°K (the temperature at which polystyrene samples melt and flow) and produced samples with trapped bubbles. Nor could we press these samples at 473°K and 5000 psi to produce a clear product. Ionox 330 (1% by weight), m.p. 590°K, sometimes produces a clear material free of bubbles, but much of the material was rejected because of the dimensional requirements of the test method.[1]

In the method finally adopted, polystyrene and the inhibitor were ground together in a Waring blender containing an inert slurrying agent. The mixed powder was dried and melted at 473°K in a vacuum oven. The time required to produce clear sheets of material was approximately four hours.

Results of impact sensitivity tests on polystyrene, pure and inhibitor-laden, are given in Table I. Both the pure polystyrene and the inhibitor-laden polystyrene were heated under the same conditions and the preliminary results indicate that no dramatic effect is to be expected.

TABLE I

RESULTS OF IMPACT TESTING OF POLYSTYRENE[a]

Drop Height, inches	Positive Trials/Total Trials	
	Pure Polystyrene	Polystyrene +0.1% Ionox 330
17.3	0/22	--
21.6	0/24	0/9
25.9	3/9	2/20
36.6	3/8	--
43.3	2/11	4/17

[a]Testing was not in complete accord with MSFC Spec 106A.

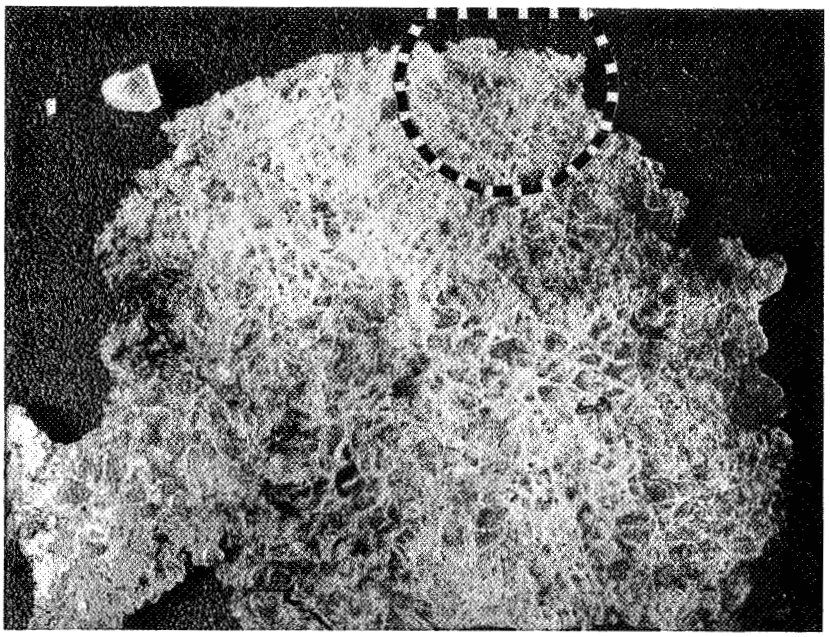
C. The Hot Spot Theory of Ignition

We concluded during the first phase of this program[3] that formation of free radicals during impact at 90°K is an important process with organic compounds but it is not governing with respect to ignitability, and formation of hot spots followed by thermal generation of radicals is the more likely mechanism.[3]

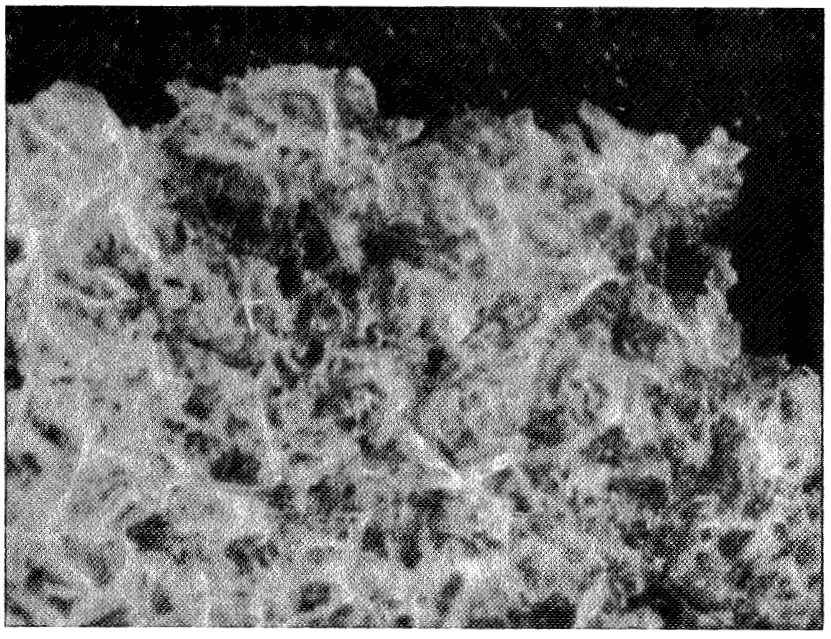
The hot spot theory is well supported by the works of Bowden and Yoffe.[4] Their work shows two important sources of hot spots in impacted samples of conventional explosives: inclusions of compressible fluids such as air or hard non-compressible solids such as grit, either of which is heated by impact pressure. A variety of materials will provide effective grit if their melting points are greater than some minimum value--350-400°C for the explosives. The hot spot theory of ignition provided a very useful working hypothesis for the study of impact sensitivity of organic materials in LOX. It also provided us with the basis for three types of hot spot experiments: impact experiments on organic materials containing grit or gaseous bubbles, experiments on samples rapidly heated with a resistance wire, and experiments on transparent samples containing opaque inclusions which are rapidly heated with a pulse of radiant energy (visible and infrared). The last type is in the exploratory phase.

1. Grit Experiments

Early in the work period we found evidence for the formation of hot spots in polystyrene wafers. A photograph of a polystyrene wafer recovered from the impact tester is shown in Fig. 3a. The product, which was a fused mass of fractured particles, was approximately 1/3 inch wide. An enlarged portion is shown in Fig. 3b. When this wafer was examined under a binocular microscope, molten charred holes could be seen near the surface at a few charred spots. In other areas of sample the char pattern appeared to follow the cracked furrows in the compacted material. Most of the material showed no evidence of charring. The entire fused mass contains small individual particles.



(a) Ca 10 X



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(b) Ca 40 X

FIG. 3 PHOTOGRAPHS OF IMPACTED POLYSTYRENE WAFER

This compacted sample (run at 25.9 inches drop height) may have resulted from rebounds rather than one impact only. The charred areas may be due to local heating from impact and they are perhaps the source of ignition and explosions. The hot spot theory seems plausible, especially when one carefully examines the impacted polystyrene wafer. It appears that a few hot spots formed and were extinguished, perhaps by oxygen starvation beyond the hot spot.

Samples of polystyrene and polyethylene (USI Chemicals Microthene F) containing 0.1 wt % silicon carbide crystals were prepared. Inasmuch as Bowden found 100 micron grit the most effective in sensitizing explosives, we chose the same size range (150 mesh, 87-104 microns). The ground polymer and silicon carbide were mixed, melted, and cooled in vacuo. This produced samples with the grit uniformly distributed in the polymer. Pure control samples were melted and cooled in exactly the same manner. Samples 50-mil thick were tested according to MSFC Spec 106A.

Results of the tests are shown in Table II and the reaction frequencies are shown in Fig. 4. Sensitivity of polystyrene is practically unaffected by the silicon carbide. The results are less conclusive for polyethylene because it is inherently less impact sensitive.

TABLE II

EFFECT OF GRIT UPON IMPACT SENSITIVITY

Impact Energy, kg-m	Positive Trials/Total Trials			
	Polystyrene m.p. = ~ 470°K [a]Tg = ~ 370°K	Polystyrene +0.1% SiC	Polyethylene m.p. = ~ 373°K Tg = 150-160°K	Polyethylene +0.1% SiC
10	15/20	19/20	0/20	2/20
8	15/20	17/20	4/20	3/20
6	13/20	14/20	3/20	1/20
4	9/20	14/20	0/20	0/20
2	6/20	3/20	--	--
1	0/20	0/20	--	--

[a]Tg = glass transition temperature.

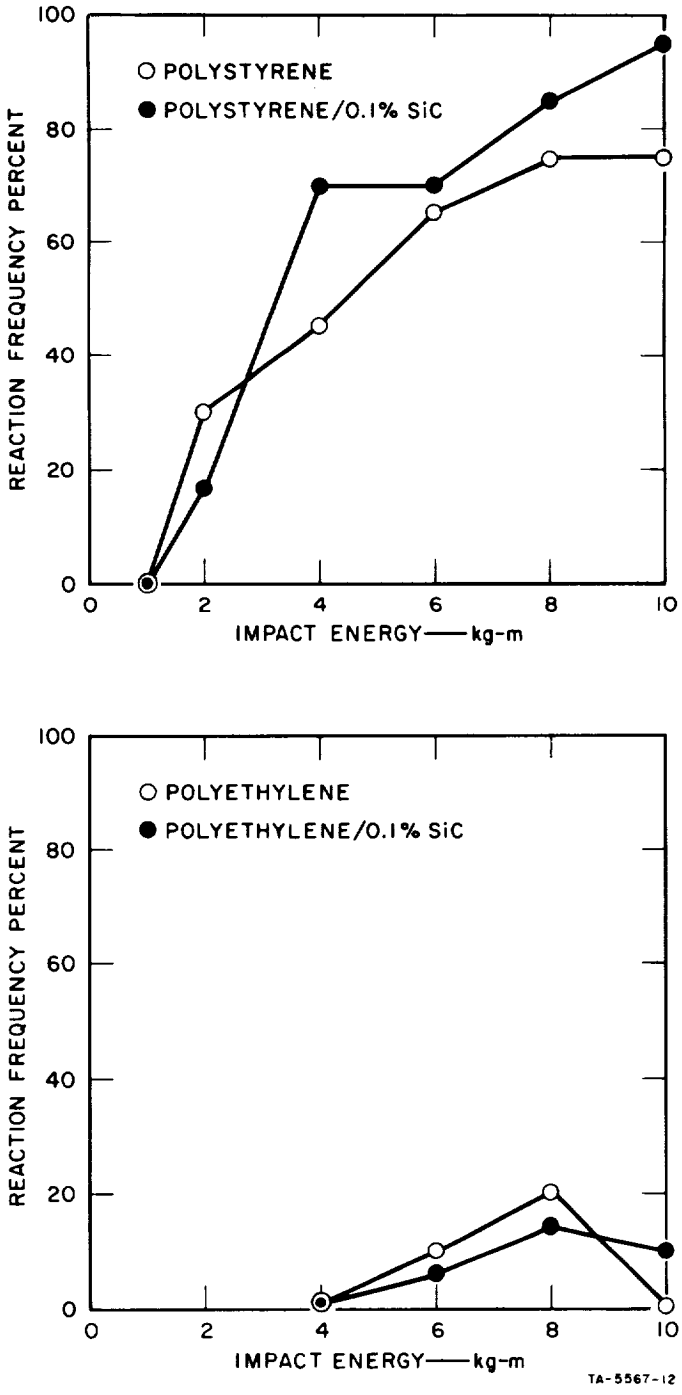


FIG. 4 IMPACT DATA FOR POLYSTYRENE AND POLYETHYLENE IN LIQUID OXYGEN

The overall results indicate that the grit is ineffective in sensitizing polyethylene and polystyrene. This suggests that these rigid glass-like polymers under impact at 90°K are themselves serving whatever role is necessary to produce hot spots--that grits are not needed.

It is important to note that only one or two of the aluminum cups were burned in this series of tests. Lucas and Riehl[6] reported that grit alone often causes the aluminum cups to react explosively. The drop height they used was not indicated.

The terms "high melting" and "low melting" are not presently definable numerically, except that, from kinetic considerations, one predicts[7] the hot spot must attain a temperature of at least ~ 270°K. Polystyrene, which is very sensitive, has a high melting point (473°K) and a high glass temperature (373°K) and, as reported[8], is not sensitized by grit. Polyethylene is insensitive, has a low melting point (~ 373°K) and a low glass temperature (150-160°K). It also appears to be too insensitive for the addition of grit to have a measurable effect:[8] its sensitivity with grit is "off-scale."

Thus we sought a low melting but impact-sensitive material: a polyethylene oil or wax would be especially suitable because of its chemical similarity to the normal polymer. We were unable to acquire any, and so mineral oil (McKesson & Robins, m.p. ~ 210°K) was used instead. Enough heavy oil was pipetted into test cups to produce a 0.05-in. thick sample. Then 150 mesh SiC (0.1 wt. %) was added on top of the oil and the samples LOX-cooled. Because of wall-wetting the final specimen thickness was about 0.017 in. Impact testing this time showed a definite and positive effect of the inclusion. At a drop height of 17.3 in. audible ignition occurred 19 out of 20 times; 13 of these positive reactions occurred on initial contact and the other 6 ignited on subsequent bounces. Neat oil, however, ignited only 10 times and only once upon initial contact.

Research by Bowden[4] and by Gross and Amster[9] has shown that hot spot sizes must be between 10 and 10^3 microns to be effective with conventional explosives. The results just described established that SiC

inclusions, ~ 100 microns, markedly sensitize mineral oil. Since particulate silica (e.g., Cab-O-Sil) is used as a filler in preparing silicone and fluorocarbon greases used at cryogenic temperatures, it was decided to investigate the sensitizing effect of this material upon mineral oil. The results are shown in Table III.

TABLE III

IMPACT SENSITIVITY OF MINERAL OIL AND MINERAL OIL CONTAINING CAB-O-SIL (17.3 inch drop height)

Cab-O-Sil	Particle Size,[a] Å	Positive Trials/ Total Trials
S-17	68	8/20
EH-5	70	13/20
H-5	85	13/30
M-5	140	13/20
COL-5	550	4/20
COL-5	550	6/20
Mineral Oil (neat)	---	5/20
Mineral Oil (neat)	---	11/20

[a]Nominal particle diameter: 1 Å = 10^{-4} microns.

Because of the possible differences between silicon carbide and Cab-O-Sil (silica) the results shown in Table III may not be directly comparable. However, the results do show no sensitizing effect of the small particles. That care must be used in interpreting these experiments is shown in the results for the duplicate control sequence with neat mineral oil. In the first set 5 out of 20 shots were positive, but in the second set 11 out of 20 were positive. In any event, the agreement of our results with the generally accepted model for conventional explosives is very good. Though the results obtained so far are preliminary, they are in accord with those we anticipated:

1. Polymer physical properties are important, viz., glass or freezing temperature.

2. Inclusion of grit sensitizes materials with low glass or freezing temperatures.

3. There is a relation between kinetic predictions and the apparent minimum impact temperature.

4. Small grit is less effective than large grit in increasing the sensitivity of susceptible materials.

2. Hot Wire Experiments

Wenograd[10] developed an apparatus for rapidly heating a narrow metal tube as a means of studying the ignition of explosives. Since it would be difficult to retain a LOX slurry of a finely divided polymer in a small diameter tube, a hot wire was used as an ignition source. Preliminary experiments with platinum wires in a LOX slurry were not very satisfactory. The wires were heated by pulses from a bank of capacitors, and the duration of the pulses was monitored on an oscilloscope. Attempts were then made to heat polystyrene films deposited from solution on the wires. This approach was not successful because of poor adhesion of the polymer film to the wire. A combination of mechanical and thermal stresses apparently caused the loss of adhesion. The insulating effect of the air on vapor film prevented heat transfer from the wire to the film, and the results of these experiments were very erratic. In the most extreme cases, the polymer film lost no measurable weight and was visibly unchanged in liquid oxygen, even though the wire was heated to redness for periods up to one second.

A series of experiments were run to obtain a hot wire system with improved heat transfer characteristics. Mineral oil (Nujol) was used as a model fuel. The design that gave reproducible results consists of a coil of 4 turns of 28 gauge Nichrome heating wire wound around a No. 54 (0.0550 in. diam.) twist drill. A small rectangular section of fine ($\sim$ 60 mesh) stainless steel screen was inserted into the coil. This arrangement allowed surface tension forces to retain the sample

after it melted, and increased the available area for heat transfer. This coil is shown schematically in Fig. 5.

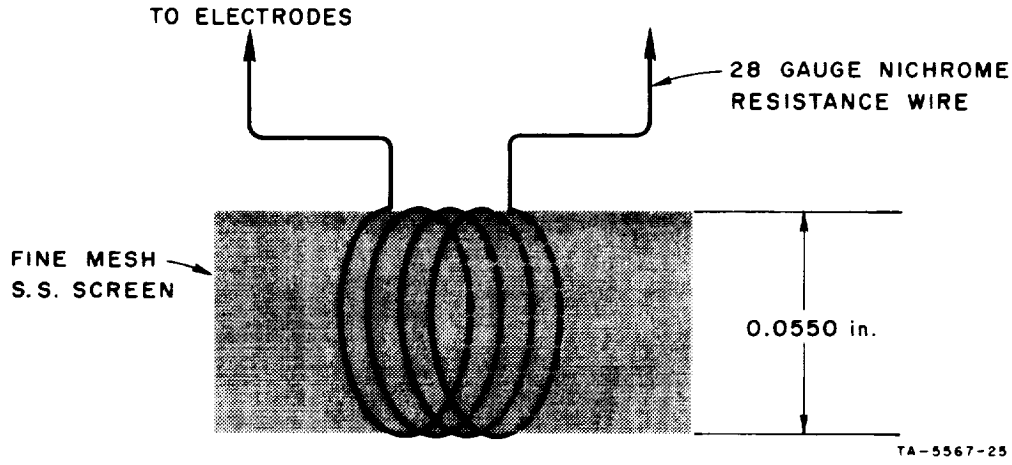


FIG. 5 SAMPLE HOLDER FOR RAPID HEATING OF DEPOSITED ORGANIC FILMS

In preliminary experiments with the modified hot wire apparatus we determined the minimum energy input, for a 0.5 sec pulse, necessary to cause reaction for a series of pure compounds. These compounds were chosen from a list supplied by Mr. C. F. Key[11] with the ABMA impact apparatus. The results are purely qualitative and must be confirmed before any attempt is made to relate them to impact sensitivity. The compounds are listed in order of decreasing thermal sensitivity: mineral oil $\tilde{=}$ n-hexyl alchol $\tilde{=}$ benzyl methyl ether $>$ benzyl alcohol $\tilde{=}$ ortho-dichlorobenzene $>$ cumene. Further, a higher energy input was required to cause reaction when the sample was submerged in LOX than when it was frozen in LOX and withdrawn to a position in the vapor of boiling oxygen ($\frac{1}{2}$ to 1 in. above the liquid surface). Combustion of the heating element occurred when organic samples burned in LOX. The wire did not become involved when samples burned in oxygen vapor.

These results indicate, strongly, that reproducibility and consistency in hot wire experiments are dependent upon reproducible heat transfer properties of the experimental setup. Further implication is that heat transfer problems are simpler in oxygen vapor than in LOX.

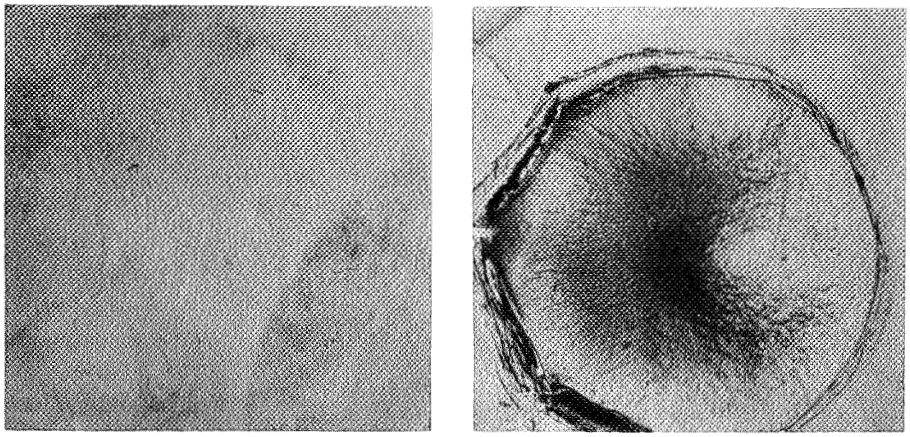
D. Photographic Studies

The use of photographic methods to study the progress of events occurring in a sample in the impact tester was inspired by the work of Wenograd.[12] Our assurance that time-resolved photography could contribute to understanding impact ignition in our systems was greatly strengthened by the report of Bowden and McOnie[13] who followed the events taking place after impact upon thin films of nitroglycerin and other explosives. Therefore, we undertook the evaluation of both still and time-resolved photography as tools for studying impact.

1. Still Photography

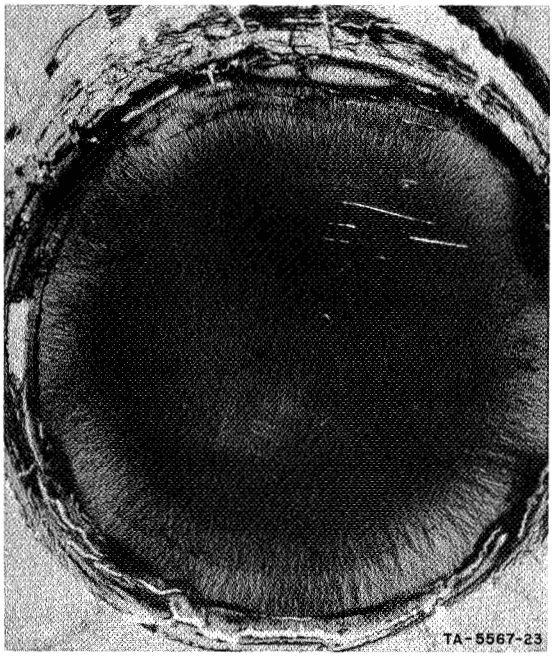
Ordinary cellulose acetate-based photographic film is much too brittle at low temperatures, and so we have used a Mylar-based emulsion: DuPont Commercial Blue-Sensitive Cronar Film. Although nominally 0.004 in., we found it to be 0.008 in. thick. Pieces of this film were placed, emulsion side up, in the impact sample cups. Over this a protective piece of $\sim$ 0.005 in. Mylar was placed. Impact tests were then conducted under liquid nitrogen and at various drop heights. Some typical results are shown in Fig. 6. At 25.9 in. and above the recovered and developed films were uniformly blackened over the entire area of contact between the film and the striker pin. Film records obtained from drops of 8.6 in. or less were only slightly blackened over a part of the central region, and the outline of the striker pin might also have been recorded. The tests showed that under these conditions the maximum useful drop height was approximately 17.3 in., for above this height the blackening due to nonreactive impact alone was too dense to permit distinguishing between it and any additional record of ignition in LOX. (This, incidentally, is a phenomenon of which Wenograd[12] seemed unaware and may invalidate some of his conclusions.)

Because of these results we conducted a large number of tests using the 17.3 in. drop height. At these heights, especially when the sample is cushioned or protected by a mica or Mylar film, ignition is improbable; thus only a few tests gave results or records which elucidated the ignition process. Some of these tests were conducted with



(a) 4.3

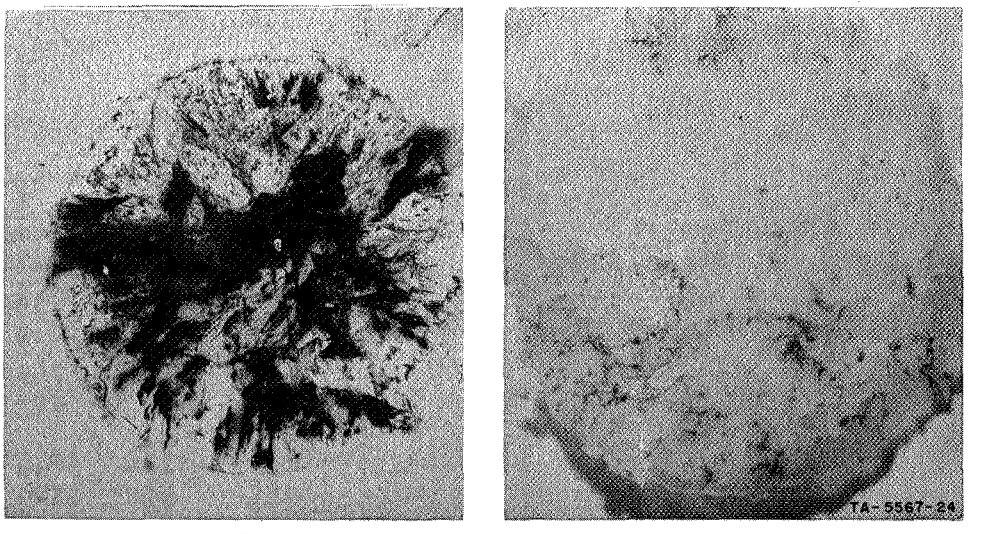
(b) 17.3



(c) 25.9

FIG. 6 TYPICAL RECORDS FROM IMPACT UNDER LIQUID NITROGEN

the photographic film at the bottom of the test cup with a thin mica or Mylar slip separating it from the striker. In each kind of test some of the developed films showed sharply delineated opaque black spots, which we attribute to nonpropagating ignition of either the polymeric film or, more likely, the gelatinous emulsion in the liquid oxygen (see Fig. 7a). During the course of these experiments we were also fortunate to recover a few specimens of impacted polystyrene with minute, discrete black spots. One such sample, a typical one but also one of the most photogenic, was obtained when no photographic film was used (see Fig. 7b).



(a) MYLAR EMULSION (b) POLYSTYRENE SPECIMEN

FIG. 7 RECORDS OF NONPROPAGATING IGNITION

We believe these results confirm our hypothesis that ignition is initiated at a number of individual sites rather than more or less uniformly within the sample. Also we recovered samples in which ignition had occurred but did not propagate; this supports the notion of a minimun critical size for hot spots--otherwise why did propagation not occur?

We also conducted tests with samples containing grit in localized segments. From these we had hoped to obtain photographic proof of the sensitization so effected. Unfortunately, the abrasive, hard properties of the grit also resulted in so many scratches on the photographs as to render them useless.

As a result of efforts to develop a transparent anvil for photographic purposes, polycarbonate materials (e.g., Lexan) were found to survive repeated impact when supported on a flat anvil. The use of a polycarbonate insert 0.25 in. thick, as shown in Fig. 8, allowed photographic film to be protected from mechanical blackening. Impact experiments were then carried out with polystyrene wafers in LOX on a polycarbonate anvil insert. In all cases where light accompanied reaction, visual detail was obscured by a general fogging of the entire film. Perhaps the transparent anvil insert for still photography may be perfected, but further work on its development has been halted.

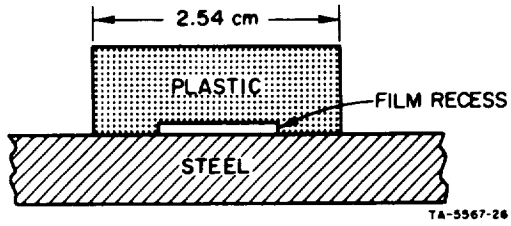


FIG. 8 POLYCARBONATE ANVIL INSERT

2. Time-Resolved Photography

Time-resolved photography of impact reactions in LOX requires two developments: a transparent anvil and an anvil block with a light path. Figure 9 is a schematic cross section of the anvil and block which are under construction. Of particular importance is the diameter of the opening below the polycarbonate anvil. The plastic anvil is destroyed when the opening is equal to that of the striker pin ($\frac{1}{2}$ in.). It was not fractured when the diameter was 3/8 in. Photography will be done with a fast action camera that can operate at speeds up to 8000 frames per second.

E. Literature Survey

Several months ago we began a literature survey to aid us in guiding our experimental program. It was the aim of this survey to acquire information describing the mechanical behavior of polymers at cryogenic temperatures, in the hope that this information would elucidate the impact ignition mechanism. We have used several excellent detailed surveys.[14-17] Literally scores of other papers were examined too.

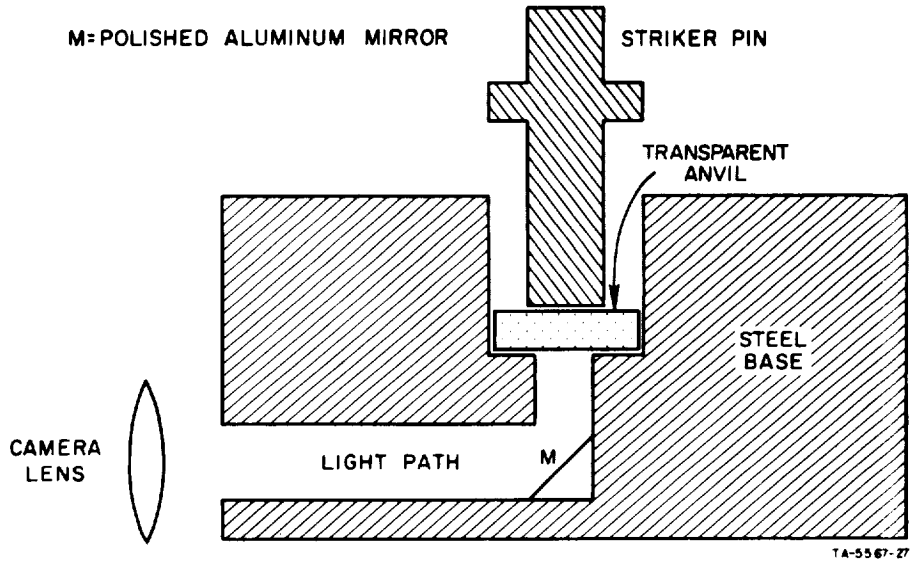


FIG. 9 SCHEMATIC OF IMPACT ANVIL ASSEMBLY FOR TIME-RESOLVED PHOTOGRAPHY

Unfortunately, we were more successful in finding what is not available than what is available. For example, there is a severe shortage of information on the thermodynamic properties of cold polymers.[18] This is probably due to the long times required for these materials to come to true thermal equilibrium below their glass temperatures. Thus, it is very difficult to analyze the thermochemistry of low-temperature oxidation processes. Similarly, though there is considerable literature about impact sensitivity,[19,21] most applies to composites, filled materials, laminates, and the like, which are of considerable practical but of little theoretical interest. However, for relatively pure materials, little information is available and this is often incomplete. In general, however, the properties of polymers depend upon increasing temperature in the following way: [14]

tensile strength compressive strength flexural strength bearing strength tensile fatigue strength tensile-compressive fatigue strength modulus of elasticity total thermal contraction strength-to-weight ratio	increases

impact strength adhesive shear strength coefficient of thermal conductivity	is variable
ductility elongation coefficient of expansion specific heat	decreases

There are some exceptions to this scheme: As temperatures decrease to the cryogenic range, tensile fatigue strength may remain the same, and elongation will decrease except for some thermosetting resin-glass fiber laminates.

It is difficult to correlate these generalizations with impact sensitivity because the properties are so interrelated, because there is a lack of useful data, and because chemistry must play a part. For example, most hydrocarbons are impact sensitive,[22] but they become less so as more tightly bound substituents, such as chlorine and fluorine, replace the relatively labile hydrogen. Thus both kinetic and thermochemical factors play a role in ordering sensitivity. We have already referred to work by Bowden,[4] and to our own attempts to initiate explosion or combustion of polymeric powder containing large quantities of free radicals.

Except for these last two there is little in the present literature to guide us and there is little information available to correlate impact results with. In short, we found no reason to modify our approach and, unfortunately, no extant data that would obviate any of our proposed experiments.

F. Discussion

The impetus for this research derived from the assumption that free radicals play an important part in the impact ignition of polymers in liquid oxygen. By the beginning of this contract year we had shown that degradation of polystyrene by grinding and ball milling at cryogenic temperatures did produce relatively large quantities of free radicals. Since then we have demonstrated that essentially equivalent radicals

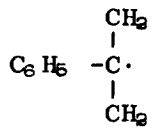
are produced by impact. Because the grinding and milling process lends itself readily to experimental control samples produced in this way were used to study their reaction with liquid and gaseous oxygen at 90°K. Inherent in our study has been the justifiable assumption that the results will also apply to the impact process. Polystyrene powder which has been exposed to air, during a particle-sizing process, has an esr spectrum indicating the presence of peroxy radicals. When the entire process is conducted in the absence of air, the spectrum is of hydrocarbon radicals; upon subsequent exposure to gaseous oxygen the spectrum is converted to that of peroxy radicals. Such peroxy radical-containing samples can be stored at 77°K for several days with little loss in spin concentration. For increasingly higher temperatures the half-life is correspondingly shorter until at 293°K the half-life is about 10 minutes.

If the presence of free radicals is sufficient to initiate ignition during LOX-impact testing one would expect that the treatment of the powders with oxygen would lead to combustion. However, admission of neither gaseous nor liquid oxygen has this result. Other than the aforementioned change in the esr spectrum the only effect of treatment with gaseous oxygen at low pressure (~ 50 torr) is that a blue flash is sometimes produced. The flash was barely detectable by eye, but it was established with an optical spectrometer that blue light was the only visible component of the radiation. This chemiluminescence seems to be similar to the disporportionation of peroxide radicals of ethyl benzene reported[23] at 333°K:

$$2\ C_6H_5\text{-}\underset{\displaystyle O_2^{\bullet}}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}\text{-}CH_3 \rightarrow C_6H_5\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_3 + C_6H_5\text{-}\underset{\displaystyle OH}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}\text{-}CH_3 + O_2 \qquad (1)$$

The luminescence spectrum of this reaction has been attributed to the return to the ground state of the excited acetophenone triplet.

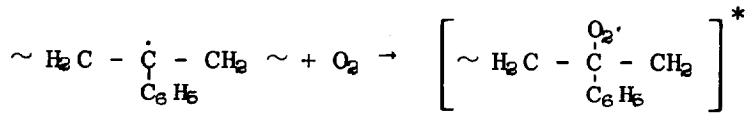
For the reaction of the polystyrene radical with oxygen the following is believed to occur: The predominant, stable free radical at 90°K is



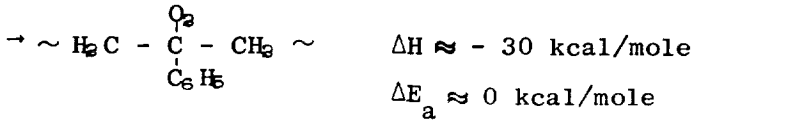
This is indicated by high energy radiation and the esr studies[24] at low temperatures.

Whether or not the radical combines with another radical and loses oxygen to become a carbonyl group or hydroxyl group depends upon the local conditions; i.e., mobility and disappearance of the peroxide are inhibited by the high viscosity. That treatment of the specimen with oxygen does not significantly change the total number of free radicals is indicated by esr measurements. For chemiluminescence only a very few of the molecules are involved.

The following sequence of reactions is proposed:



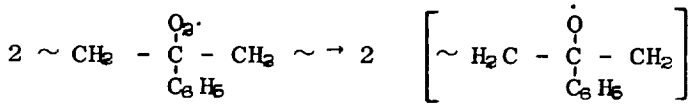
(2)



$\Delta H \approx -30$ kcal/mole

$\Delta E_a \approx 0$ kcal/mole

This sequence may be followed at higher temperatures by the reaction:



(3)

The final state of the bracketed portion in reaction 3 is unknown at 90° K.

Observation of blue light, which corresponds to approximately 35-80 kcal, is evidence that the transition to the triplet state of a "styryl carbonyl" or equivalent structure has occurred. Reaction 2 is not sufficiently energetic to produce blue light, but oxidation involving

peroxides and the loss of O_2 is.[25] This appears to confirm that free radicals can be involved in the oxidation process at low temperature.

From these studies it was concluded that free radicals are very likely involved in ignition but that their presence is not sufficient. Accordingly, attention has been directed toward examining the applicability of Bowden's hot spot theory of explosive initiation[4] to this situation. The essence of the theory is that some of the energy of impact is converted to thermal energy by various mechanical (viscous, frictional, etc.) processes which result in the heating of a relatively few foci within a reactive sample. If these hot spots rise to a high enough temperature, spontaneous rapid decomposition ensues; this is because heat is no longer lost as rapidly as it is produced. The result is that reaction originates in a few locations but rapidly propagates to consume the sample. A requirement is that the hot spot temperature be high enough for propagating self-heating. Bowden found that the inclusion of hard, high melting point grit sensitized an explosive. When the grit melting point was lower than the temperature required for thermal explosion it had no effect on sensitivity. During much of this year we have conducted experiments to show that a similar line of reasoning applies to the LOX impact situation. The impact machine was modified so that photographic records might be obtained. These showed that ignition does not originate uniformly through the sample but rather does so at a few isolated points. The recovery of a few severely fractured impacted samples with one or two very black carbonaceous spots was additional evidence. Apparently the heat evolved by limited reaction at the hot spot was less than that carried away and combustion was incomplete. One can speculate that liquid oxygen, under some circumstances, is too good a heat sink and that, perhaps, ignition occurs more readily in gaseous oxygen.

A number of experiments were performed using polymers to which high melting grit was added. Polystyrene which has a high melting point was unaffected; mineral oil (m.p. $\sim 210^{\circ}K$) was definitely sensitized. From the prediction that a temperature of approximately $270^{\circ}K$ is required (c.f. Sec. III-E.5) for the onset of chain oxidation in polystyrene-like

molecules we can assume that hot spots must attain that temperature before impact ignition can propagate. Our results are consistent with this conclusion, for, obviously, polystyrene can serve as "its own grit," but the oil "needs help." In more elegant terminology, all other things being equal, low melting or glass-transition points favor insensitivity.

For a more positive justification for interpreting LOX-impact sensitivity test results in terms of Bowden's model, we are studying the results of abruptly heating hydrocarbon samples in the absence of mechanical forces and are using electrical heating to achieve this result. At this stage only preliminary results are available, but they do show that heat transfer from the hydrocarbon-oxygen interface is important: Under certain conditions ignition occurs in gaseous but not liquid oxygen.

We are continuing the experiments with heated samples and are modifying the impact machine to obtain high speed motion pictures of sample fracture and ignition propagation.

III REACTIONS OF CARBON RADICALS WITH OXYGEN AT LOW TEMPERATURES

A. Background

This portion of the study is concerned with the chemistry of carbon free radicals and oxygen at low temperature, and particularly with the interactions of peroxy radicals to form intermediate polyoxides and the characterization of these compounds.

$$2RO_2\cdot \rightleftarrows RO_4R \text{ (tetroxide)} \qquad (1)$$

$$RO_2\cdot + RO\cdot \rightleftarrows RO_3R \text{ (trioxide)} \qquad (2)$$

In the first annual report[3] we described the general technique for generating peroxy radicals at low temperatures by photolysis of azoalkanes in the presence of dissolved oxygen. Experiments with azoisobutane (AIB) in methanol and pentane at 143 - 178°K showed that an unstable tetroxide or trioxide was formed at these temperatures. On warming to above 190°K this polyoxide decomposed with evolution of oxygen.

Photolysis of AIB solutions with or without oxygen produced an unstable yellow material which decomposed above 243°K to form nitrogen and t-butyl radicals. Azobisisobutyronitrile (ABN) also forms an unstable yellow photoproduct which evolves nitrogen above 243°K.

Since then we have investigated the AIB-oxygen system in more detail, obtaining more complete product analyses and some kinetic measurements on oxygen evolution. Similar studies have been carried out with t-butyl iodide (TBI) and oxygen and trifluoromethyl iodide (TMI) and oxygen. A structure proof for the yellow photoproduct from AIB is presented.

B. Summary

The photolysis of AIB and oxygen in $CFCl_3$ at 173 - 193°K gives in part products of cage interactions of t-butyl radicals (isobutane,

isobutylene, and a little C_8H_{18}). Some of the t-Bu· radicals that react with oxygen appear as an unstable intermediate believed to be di-t-butyl trioxide. This intermediate decomposes to give oxygen with a half-life of 30 minutes at 196°K and an apparent activation energy of 12 ± 2 kcal/mole.

The photolysis of TBI and oxygen in CF_3Cl at 163 - 298°K gives t-butyl alcohol, t-butyl hydroperoxide, and isobutylene, with no evidence for an unstable, oxygen-evolving intermediate. These results suggest that the photolysis gives both t-Bu· + I· and isobutylene + HI, and that the HI converts the t-BuO· and $t\text{-BuO}_2$· radicals to alcohol and hydroperoxide, preventing their interaction to give trioxide.

Photolysis of TMI and oxygen in $CFCl_3$ near 173°K produces COF_2, CO_2, and SiF_4, but neither a bis-trifluoromethyl polyoxide nor peroxide was formed. A reaction between iodine and CF_3O· is thought to be responsible for the absence of polyoxides and peroxide.

The unstable yellow photoproduct from AIB below 223°K has been identified as the cis isomer. This isomer decomposes in the dark at 235°K to give about 80% of the original trans isomer and about 20% of reaction products of caged t-butyl radicals.

Two NASA-supplied samples of fluorosilicone grease have been examined by spectroscopic and microscopic methods. No significant chemical differences have been found, although the samples have markedly different viscosities. Optical microscopy shows that one sample has globules of silicone fluid free of silica thickener; the other sample has no fluid globules.

C. Experimental Procedures

The vacuum line and photolysis source were described in the first annual report.[3] Experiments with AIB were carried out in the reaction cell also described there. A portion of the chilled (273°K) reaction mixture was then transferred to an nmr tube and total products were estimated using an internal standard. This technique led to some loss of volatile products and did not permit low temperature nmr measurements on reaction mixtures before the cell contents were warmed.

A new reaction cell with a magnetically driven glass stirrer was used for reactions of TBI and TMI. The cell is a cylinder 15 cm long by 4 cm in diameter which can be disconnected from the vacuum line and inverted in the coolant bath to transfer all of the cell contents (~ 1 ml) into an nmr tube sealed onto one side of the cell. Thus complete transfer of the reaction mixture to an nmr tube was carried out at 193°K or lower after which the nmr tube, sealed off from the cell, could be kept at 200°K while the nmr spectrum was run.

D. Results

1. t-Butyl Radicals and Oxygen

In some earlier (unreported) photolyses with AIB and 200-300 torr oxygen, analyses of the reaction mixtures indicated substantial amounts of isobutane and isobutylene despite what we considered an agitation rate adequate to oxygenate all t-butyl radicals. In an effort to convert most t-butyl radicals to t-butyl peroxy radicals, experiments were performed with higher oxygen pressures at lower temperatures to increase oxygen solubility, and in liquid ethane solvent to minimize viscosity effects.

The photolyses of AIB with oxygen were carried out at 143°K with 1100 torr oxygen and at 164°K with 1520 torr oxygen. Nitrogen evolution (from AIB) was measured at the reaction temperature and again at room temperature. Oxygen evolution was measured at several low temperatures and the stable reaction products were determined by nmr, glc, and titration. The experiments at 143°K were carried out in liquid ethane, but the ethane was subsequently replaced with $CFCl_3$ at 183°K. Experiment 96 at 164°K was carried out entirely in $CFCl_3$. Results are given in Table IV.

Experiments 93 and 94 show very good balances for t-butyl groups in the AIB decomposed and experiment 96 for the nitrogen evolved. Some discrepancies are undoubtedly due to the difficulty in quantitative transfers of these volatile mixtures, particularly the isobutane and isobutylene. The source of the hydroxylic hydrogen in experiments 93

and 94 is puzzling: below 173°K the only obvious source is the large excess of ethane (or ethylene impurity therein); at 210°K and 190°K (where ethane had been replaced by $CFCl_3$), the only obvious source is the azo compound or its decomposition products.

TABLE IV

PHOTOLYSIS OF AIB AND OXYGEN

Conditions and Results	Experiment Number		
	93	94	96
Temperature, °K	143	143	164
Time, min	1080	540	
Solvent	ethane	ethane	$CFCl_3$
Reactants			
AIB, μmoles	212	215	1235
moles/liter	0.0132	0.0135	0.130
O_2, torr	1100	1100	1520
Gas evolved, μmoles			
N_2[a]	107, 1	176, 7	81, 24
O_2[b]	40, 210°K	60, 190°K	17, 196°K
Products, μmoles by nmr or glc			
	nmr	nmr	glc
t-BuOH	133	21	0
t-BuO_2H[c]	24	50	0
$(CH_3)_2CO$	4	2	0
t-Bu_2O_2	22	23	12
i-C_4H_8	60	54	80
i-C_4H_{10}	63	54	85
C_8H_{18}	10	9	--
Unknowns[d]	--	100	--
Σt-Bu in products	348	345	189
ΔAIB	176	188	--

[a] First value is N_2 evolved at reaction temperature, second is N_2 evolved at room temperature from decomposition of cis-AIB (see Section II-D-4).

[b] Measurement at temperature specified.

[c] Analyzed by Wibaut iodometric titration.

[d] As t-butyl groups.

From Table IV less than two-thirds of the t-butyl residues found were oxygenated, 13% in experiment 96. The following argument points to considerable cage combination of t-butyl radicals. Since dimerization of 2t-Bu· radicals is minor, reactions 3 and 4 are the principal reactions.

$$t\text{-Bu}\cdot + O_2 \rightarrow t\text{-BuO}_2\cdot \qquad (3)$$

$$2t\text{-Bu}\cdot \rightarrow i\text{-}C_4H_{10} + i\text{-}C_4H_8 \qquad (4)$$

$$\frac{\Delta t\text{-BuO}_2\cdot}{\Delta iC_4H_8} = \frac{k_3[O_2]}{k_4[tBu\cdot]}$$

Thus the proportion of radicals that react with oxygen is a function of both oxygen and t-Bu· radical concentrations. Using values of $k_3 \sim 10^9$ liter/mole/sec[26a] and $k_4 = 10^{9.5}$ liter/mole/sec[26b] gives a ratio of 0.3 for k_3/k_4; for $[O_2] = 0.01$ mole/liter, the [t-Bu·] must be 0.003 mole/liter in order that just 33% of the radicals become oxygenated. This high concentration of t-Bu·, one-third the initial AIB concentration, could not be attained in any ordinary photolysis and suggests that most of the disproportionation products ($i\text{-}C_4H_{10}$ and $i\text{-}C_4H_8$) arise from cage recombination of t-butyl radicals generated in close proximity to one another from photoexcited cis-t-AIB (III-D.4).

Corroborative evidence for this view is provided by the observation that almost equal amounts of isobutane and isobutylene are formed in each experiment. If there were a significant number of uncaged t-butyl radicals available, we would expect them to react with peroxy or alkoxy radicals to give more isobutylene than isobutane as well as hydroperoxide and alcohol.

Rates of oxygen evolution, measured at the indicated temperatures, were plotted as first-order rates of formation (log O_2 vs time). The data from run 93 at 210°K and run 96 at 196°K gave good straight lines: $k_1^{210^\circ} = 8 \times 10^{-4}$/sec; $k_1^{196^\circ} = 10^{-4}$/sec; however, these values give an A factor of $10^{9.5}$ and an activation energy of 12 kcal/mole for oxygen evolution. Benson[27] has estimated bond dissociation energies DH(O-O) of 5 ± 12 kcal/mole for tetroxides and 20 ± 6 for trioxides. Thus the

measured activation energy of 12 kcal/mole, if equivalent to the bond dissociation energy of a polyoxide, is consistent with either polyoxide structure or a mixture of both polyoxides, but the A factor is unreasonably low for a unimolecular reaction. The rate constants are suspect and will require careful remeasurement.

2. Photolyses of TBI with Oxygen

The difficulties in obtaining high conversions of t-butyl radicals to t-butyl peroxy radicals in experiments using AIB as the radical source prompted us to study the photolysis of TBI as an alternate source of radicals.[38] Since the carbon radicals are generated one at a time from TBI, t-butyl cage recombination of carbon radicals is no longer possible and better yields of peroxy radicals might result. However, the reaction proved to be complicated by the I_2 and HI formed.

Commercial samples of TBI (K and K Laboratories) were vacuum-distilled from silver powder, diluted to 1 mole/liter in $CFCl_3$, and stored at 273°K. The solutions have a weak UV absorption tail extending beyond 3100 Å, with the principal band centered around 2700 Å. TBI decomposes during gas chromatography on a Carbowax 20M column if the temperature is much above 40°K; below this temperature resolution of product mixtures is poor. For this reason we have relied mostly on analyses of products by nmr. TBI has a single nmr absorption band at τ 8.09, well downfield from the chemical shift positions of products expected from oxidation of t-butyl radicals (see Fig. 10).

Results of six experiments with TBI and oxygen in $CFCl_3$ at 163-298°K are shown in Tables V and VI. The experiments at 163 and 178°K in Table V, with otherwise similar conditions of concentration and time, gave the same conversions (about 15%) and only four detectable products: isobutylene, t-butyl alcohol, t-butyl hydroperoxide, and iodine (not determined). Neither experiment evolved any oxygen, indicating the absence of polyoxide intermediates. The room temperature experiment gave 90% conversion, mostly to t-butyl alcohol, iodine, and to a little isobutylene. Experiments 116 and 119 in Table VI were done in the improved reaction cell described above, analyzed by nmr, and titrated for hydroperoxide, iodine, and HI (acid titration). These analyses gave good material balances for both iodine and t-butyl groups.

A surprising feature of this system is the presence of both hydroperoxide and HI, which under most conditions would react immediately to form water, alcohol, and iodine. The stability of this mixture probably results from both the non-polar medium and the low concentrations of products.

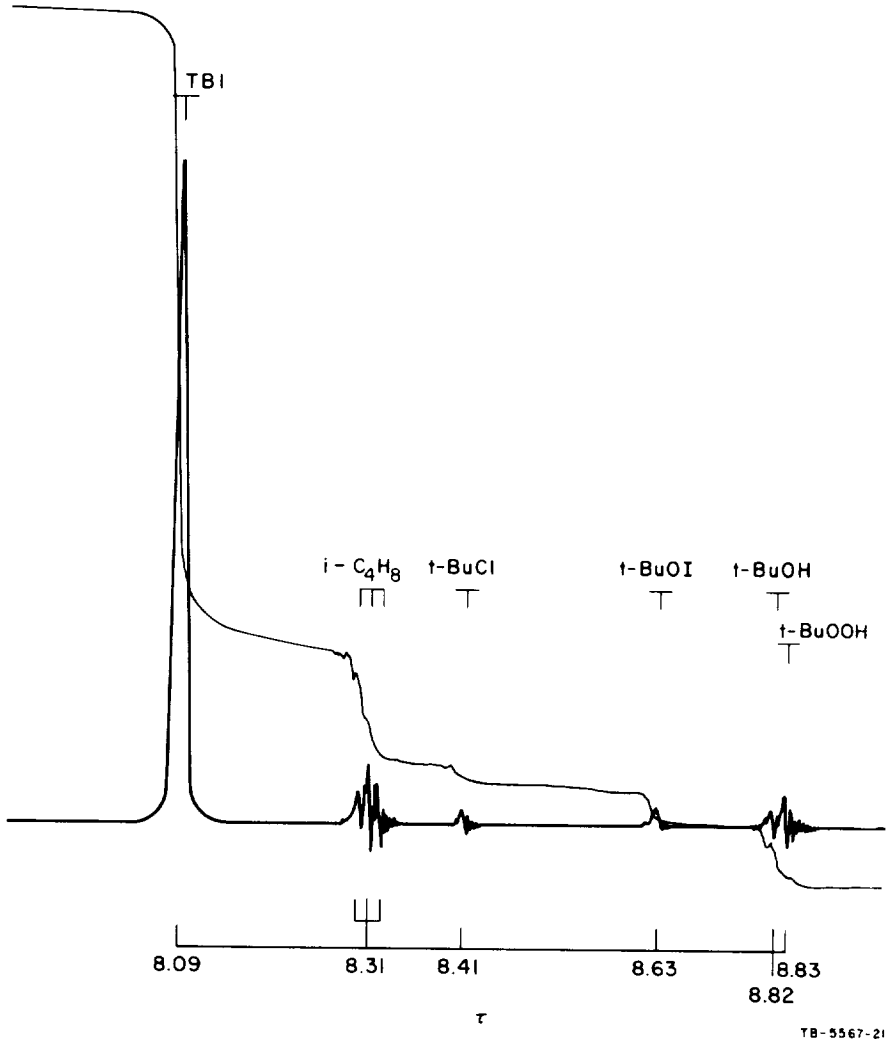


FIG. 10 NMR SPECTRUM OF PHOTOLYSIS PRODUCTS OF tBuI AND O_2 AT 173°K IN $CFCl_3$

TABLE V

PHOTOLYSIS OF TBI AND OXYGEN IN $CFCl_3$

Conditions and Results	Experiment Number			
	101	102	106	97[a]
Temperature, °K	178	163	298	173
Time, min	240	240	240	900
Reactants				
TBI, μmoles	620	760	580	234
moles/liter	0.10	0.13	0.11	0.10
O_2, torr	880	880	880	1000
Products by nmr, μmoles				
ΔTBI	100	130	511	50
i-C_4H_8	29	58	34	21
t-BuOH + t-BuO_2H	63	66	280	24
Unknowns	--	--	41 + 96[b]	45
Σt-Butyl in products	92	124	451	45

[a]Used light of 3000-4000 Å.

[b]Counted as t-Butyl groups.

The products from TBI lack entirely the isobutane, C_8H_{18}, and oxygen-evolving intermediate found in the AIB products. The excess of hydroxylic hydrogen in experiments 101 and 106 is probably experimental error, since the material balances here preclude satisfactory accounting. These results suggest that photolysis of TBI is represented by the overall reactions.

$$\text{t-BuI} \overset{h\nu}{\rightleftharpoons} \text{i-}C_4H_8 + \text{HI} \qquad (5)$$

$$\text{t-BuI} \rightleftharpoons \text{t-Bu}\cdot + \text{I}\cdot \qquad (6)$$

$$\text{t-Bu}\cdot + \text{I}\cdot \rightarrow \text{i}C_4H_8 + \text{HI} \qquad (7)$$

TABLE VI

PHOTOLYSIS OF TBI AND OXYGEN
IN $CFCl_3$ AT 173°K

Conditions and Results	Experiment Number	
	116	119
Time min	1800	1440
Reactants		
TBI, μmoles	230	290
TBI, moles/liter	0.15	0.15
O_2, torr	980	1100
Products[a] by nmr, μmoles		
ΔTBI	63	45
i-C_4H_8	39	25
t-BuOOH[b]	10	5
t-BuOH	4	2.5
t-BuCl	4	0
t-BuOI	5	5
I_2	19	16
HI	20	2
Σt-Bu in products	62	38
ΣI in products	63	37
Percent Conversion	27	15

[a]Analyses have an estimated precision of ± 10%.

[b]By iodometric titration.

The formation of oxygenated products depends on the ability of

$$t\text{-Bu}\cdot + O_2 \rightarrow t\text{-BuO}_2\cdot \qquad (3)$$

to compete with reactions 6 and 8.

$$t\text{-Bu}\cdot + I_2 \rightarrow t\text{-BuI} + I\cdot \qquad (8)$$

Many of the $t\text{-BuO}_2\cdot$ radicals must react by

$$2t\text{-BuO}_2\cdot \rightarrow 2t\text{-BuO}\cdot + O_2 \qquad (9)$$

because use of HI for reduction of $t\text{-BuO}_2\cdot$ radicals would yield too much isobutylene. The $t\text{-BuO}\cdot$ and remaining $t\text{-BuO}_2\cdot$ radicals are scavenged by HI:

$$t\text{-BuO}_n\cdot + HI \rightarrow t\text{-BuO}_n H + I\cdot \qquad (10)$$

If consumption of HI in reaction 10 limits the extent to which reaction 5 can proceed, and since reactions 6 and 8 consume all the $t\text{-Bu}\cdot$ radicals which do not react by 3, reaction 3 largely controls the net decomposition of TBI. There should be about 5 mole % of $t\text{-Bu}_2O_2$ (not detected) accompanying the t-BuOH.

Isobutylene, a major product from TBI-O_2 systems, could also be formed in another way:

$$t\text{-Bu}\cdot + t\text{-BuO}_2\cdot \not\rightarrow i\text{-}C_4H_8 + t\text{-BuO}_2H \qquad (11)$$

$$t\text{-Bu}\cdot + t\text{-BuO}\cdot \not\rightarrow i\text{-}C_4H_8 + t\text{-BuOH} \qquad (12)$$

We reject these reactions on the basis that since comparable amounts of the three products formed in reactions 11 and 12 are found, there should also be a considerable number of interactions between like radicals and particularly

$$2t\text{-}Bu\cdot \rightarrow + \; i\text{-}C_4H_{10} + i\text{-}C_4H_8 \qquad (4)$$

Absence of isobutane (C_4H_{10}) among the products indicates reactions 11, 12, and 4 are not important under these conditions, and isobutylene is produced largely or entirely via 5 and 7. From this argument it then follows that all free t-butyl radicals produced are efficiently scavenged only by oxygen or iodine radical--a premise that prompted the original investigation of this system.

3. Photolysis of TMI and Oxygen

Many organic compounds that are both useful and relatively safe under LOX conditions contain carbon-fluorine bonds. It was therefore of considerable interest to study the reaction of one or more organic fluorine radicals with oxygen at low temperatures. We chose the trifluoromethyl radical for the initial study because it is the simplest of the series and is easily generated by photolysis of trifluoromethyl iodide (TMI).[29]

Heicklen[30] has studied the photolysis of TMI with oxygen at 298°K and has reported carbonyl fluoride as the only product. Although neither fluorine nor iodine were detected, they must have been formed.

$$CF_3I \xrightarrow{h\nu} CF_3\cdot + I\cdot \qquad (13)$$

$$2I\cdot \rightarrow I_2 \qquad (14)$$

$$CF_3\cdot + I_2 \rightarrow CF_3I + I\cdot \qquad (15)$$

$$2CF_3\cdot + O_2 \rightarrow 2CF_2O + F_2 \qquad \text{(2 steps)} \qquad (16)$$

In the absence of some radical scavenger such as oxygen, the photolysis is self-inhibiting because of reaction 15.

Five runs were made with TMI in $CFCl_3$ with 1000 torr oxygen around 163°K using Pyrex or quartz cells. Oxygen evolution was measured at 200°K and 273°K. Product analyses were done by F^{19} nmr and by titration for iodine. The results in Table VII show that small and reproducible

conversions of TMI can be effected (as shown by formation of iodine). However, neither F^{19} nmr nor glc revealed the presence of the organic fluorine products that must accompany iodine (small amounts of fluorinated impurities were detected). Oxygen evolution was, with one exception, very small or absent. The disparity between apparent oxygen evolution and iodine formation is so great that we attribute the oxygen evolution to an experimental error.

TABLE VII

PHOTOLYSIS OF TMI AND OXYGEN[a] in $CFCl_3$
AT 163°K

Experiment	Time min	TMI moles/liter	TMI μmoles	Evolved O_2 at >200°K μmoles	I_2 Formation by Titration μmoles
105[b]	180	0.092	553	6	4
106[b]	1440	2.2	13,350	5	240
107[c]	900	0.14	322	46	--
108[c]	900	0.16	330	0	14
109[c]	900	0.16	330	0	14

[a] At 1000 torr.

[b] Pyrex cell.

[c] Quartz optics and cell.

Authentic samples of the bis-(trifluoromethyl)peroxide, $(CF_3)_2O_2$, and carbonyl fluoride, COF_2 (the products expected from oxidation of CF_3) have been examined by F^{19} nmr. The peroxide nmr band (singlet) is at $\varphi = 70$;* COF_2 is at $\varphi = 20.3$. In both cases, the bands lie close to the strong 2000 cps sidebands generated from the solvent $CFCl_3$ band at $\varphi = 0$. Thus these two compounds would go undetected in this solvent and this probably accounts for their apparent absence in the reaction.

* φ is the chemical shift in ppm of fluorine bands from the standard band of $CFCl_3$ at $\varphi = 0$.

Since both products are reactive gases with characteristic and unique IR bands,** IR spectrophotometry appeared to be an alternate analytical technique. Therefore, several calibration experiments were done with mixtures of peroxide, COF_2, and $CFCl_3$ (the reaction solvent) in a 10 cm gas cell (56 ml volume) with NaCl optics using a Perkin-Elmer Model 221 infrared spectrophotometer. About 0.1 μmole of either product can be detected under these conditions.

Two reaction mixtures from a 16 hr photolysis of 0.2 mole/liter TMI in $CFCl_3$ at 173°K were analyzed by IR spectrophotometry and by iodine titration. In both cases only CF_2O, CO_2, and SiF_4 were detected; however, carbon and fluorine balances were very poor indicating some fault in the analytical procedure.

A third run (129) with 0.23 mole/liter TMI was made and analyzed by nmr for remaining TMI, by IR for products and by titration for iodine. In this case the IR analyses were done using a compensating gas cell to remove solvent bands and to improve the SiF_4 analyses. Results, in Table VIII show that almost one-fourth of the $CF_3\cdot$ radicals are oxidized to CO_2 and three fourths to COF_2 with no detectable amount of peroxide. The remaining fluorine is found as SiF_4, also detectable in the IR. The carbon, fluorine, and iodine balances are good.

The interesting result that comes out of these experiments is that no bis(trifluoromethyl) peroxide is formed even though oxidation of the trifluoromethyl radicals seems complete (no dimer, C_2F_6, has ever been detected by nmr). We conclude therefore that trifluoromethoxy radicals are converted in some way to carbonyl fluoride before they can dimerize to peroxide. The most plausible scheme is

$$CF_3I \xrightarrow{h\nu} CF_3\cdot + I\cdot \qquad (13)$$

$$CF_3\cdot + O_2 \rightarrow CF_3O_2\cdot \qquad (17)$$

** CF_2O has a carbonyl band at 5.20 μ; $(CF_3)_2O_2$ has a moderately strong C-O stretch at 7.80 μ. Both of these bands are free from interference from $CFCl_3$ bands.

TABLE VIII

PHOTOLYSIS OF TMI AND OXYGEN IN $CFCl_3$ at 173°K

Conditions and Results	Experiment 129
Time, min	1200
Reactants	
TMI, μmoles	321
moles/liter	0.23
O_2, torr	
Products by IR, μmoles	
COF_2	27
CO_2	10
SiF_4	15
I_2	18[a]
ΔTMI	41[b]
ΣC in products	37
ΣF in products	114

[a]By iodometric titration.

[b]By nmr.

$$2CF_3O_2\cdot \rightarrow 2CF_3O\cdot + O_2 \qquad (18)$$

$$CF_3O\cdot + I\cdot \rightarrow CF_2O + IF \qquad (19)$$

$$2CF_2O + \text{glass} \xrightarrow{\sim 298^\circ K} 2CO_2 + SiF_4 \qquad (20)$$

Reactions 17 to 19 are similar to those written for t-Bu· radical and oxygen. Reaction 19 provides an exothermic path (-15 kcal/mole) for conversion of $CF_3O\cdot$ radicals to CF_2O. If $CF_3O\cdot$radicals are removed from the reaction quickly by reaction 19, they cannot react with $CF_3O\cdot$ radicals to form $CF_3O_3CF_3$, thus explaining the lack of delayed oxygen evolution.

Thus this system resembles the t-butyl iodide system where HI converts t-butoxy radicals to alcohol before they react with $t\text{-}BuO_2\cdot$ radicals to form t-butyl trioxide.

4. Structure of AIB Photoproduct.*

Almost from the beginning of this project we have, from time to time, attempted to determine the structure of the unstable yellow nitrogen compound produced by photolysis of ordinary trans-AIB at temperatures below 210°K. Although the physical and chemical evidence previously obtained suggested that the photoproduct is di-t-butyl tetraazadiene ($t\text{-}BuN_2N_2t\text{-}Bu$), instability of the intermediate prevented an accurate determination of the ratio of t-butyl groups to nitrogen.

We now report the results of chemical studies and of accurate low-temperature nmr measurements on the formation and decomposition of this compound; together, these provide strong evidence that the yellow compound is cis-AIB. The success of the nmr experiment is due in part to a simple all-glass stopcock, sealed to the end of the nmr tube, that allows one to analyze for gas on the vacuum line without interfering with nmr measurements.

An nmr tube containing a degassed solution of 108 μmoles AIB, in ~ 1 ml $CFCl_3$ was irradiated at 178°K using a narrow-pass filter (Corning 7-84, cutoff at 4000 Å) to minimize photolysis of the intermediate. Nitrogen evolution was measured; the valve on the nmr tube was closed, and the nmr spectrum was measured and integrated at 207°K. The contents of the tube were then warmed to 235°K, held there overnight (yellow color disappeared), and the nmr spectrum was rerun at 207°K to minimize any temperature effects on the spectrum. Afterward, nitrogen evolution was again measured. Since the total number of protons in the system was fixed, the absolute amount of each product and the distribution of t-butyl groups were calculated from the integrated spectrum without the use of an internal standard (Fig. 11).

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*Work described in this section was supported by Stanford Research Institute; it is reported here to provide continuity with earlier reports[3] of work on this compound.

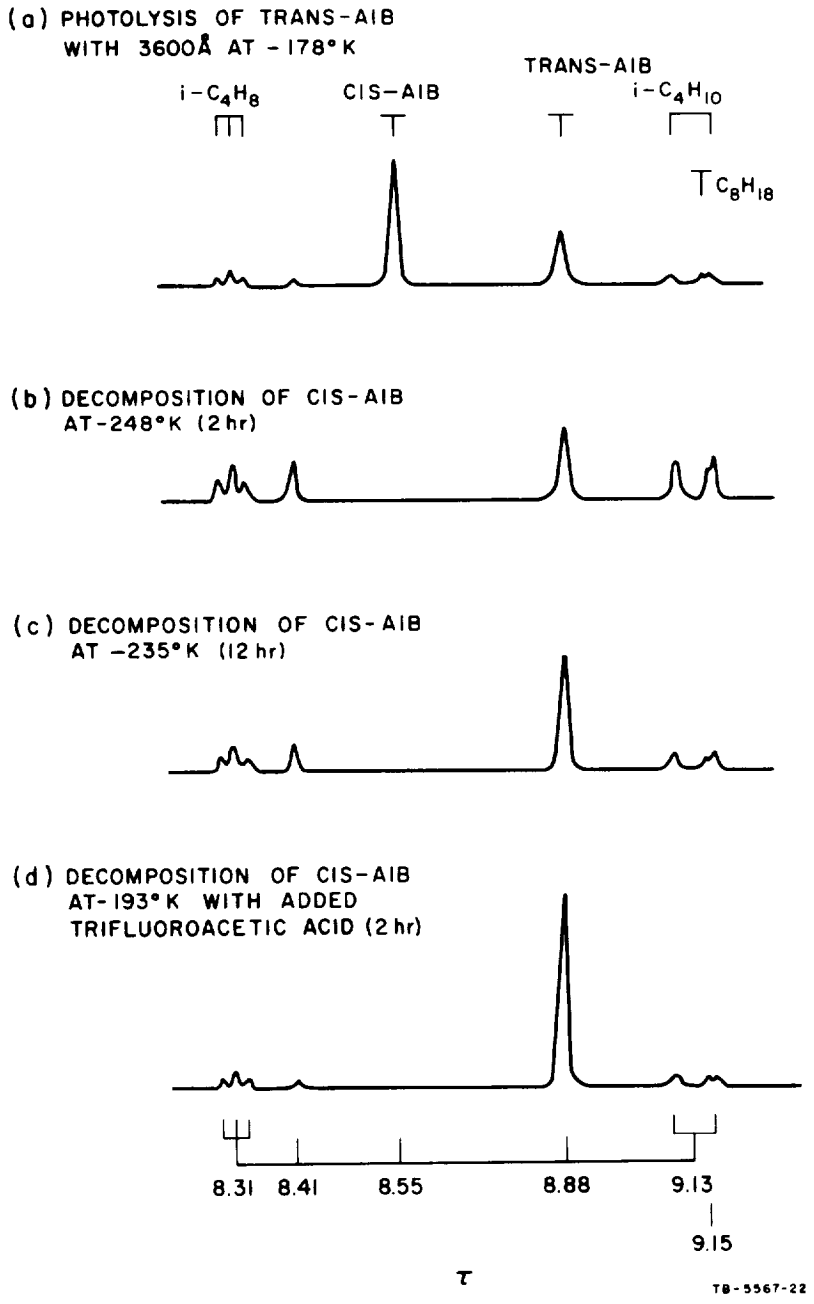


FIG. 11 NMR SPECTRA OF CIS AND TRANS -t-Bu_2N_2 AND DECOMPOSITION PRODUCTS IN $CFCl_3$

Results (Table IX) show that AIB was converted to the intermediate in 83% yield with little formation of nitrogen or t-butyl radicals. On warming, most of the AIB was reformed. All of the nitrogen and > 92% of the t-Bu groups are accounted for. The experiment shows that the product has a composition corresponding to $(R_2N_2)_x$ (isomeric with R_2N_2 when x = 1) and not R_2N_4 as previously thought.

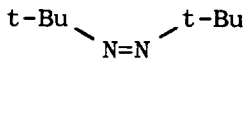
TABLE IX

FORMATION AND DECOMPOSITION OF CIS-AIB

Reactants and Products	Fraction of Total t-Butyl Groups and Nitrogen[a]
Photolysis at 178°K	
Reactant: trans-t-Bu_2N_2	1.00
Products	
trans-AIB	0.25
cis-AIB	0.62
i-C_4H_8	0.055
i-C_4H_{10}	0.065
C_8H_{18}	0.0028
N_2	0.15
Decomposition at 235°	
Reactant: cis-AIB	0.62
Products	
trans-AIB	0.50
i-C_4H_8	0.033
i-C_4H_{10}	0.048
C_8H_{18}	0.014
t-BuCl	0.026
N_2	0.13

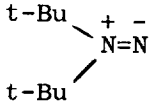
[a]Original solution contained 108 μmoles AIB in ~ 1 ml $CFCl_3$.

The bright yellow color (λ_{max} 4400 Å) and facile reaction of the intermediate with tetracyanoethylene at 223°K to give a deep red, unstable complex suggest that this product is one of the two isomers of AIB rather than a polymer:



cis-AIB

(I)



1,1-di-t-butyldiazine

(II)

To distinguish between the two isomers we have examined the effect of dilute (0.005 mole/liter) trifluoroacetic acid on the photo-isomer at 193°K, where the isomer is otherwise stable. Under these conditions the photoproduct isomerized cleanly to trans-AIB, confirming its identity as the cis isomer. Isomer (II) would be expected to cleave to isobutane, isobutylene (or t-butyltrifluoroacetate), and nitrogen by an ionic mechanism.

When nearly colorless AIB photolyzes in Pyrex below 213° with light of < 4000 Å wavelength, it is cleanly converted to the bright yellow cis isomer. When unfiltered mercury light is used, most of the AIB is converted to nitrogen and t-butyl radicals and only a small steady-state concentration of cis-AIB. Oxygen does not affect either process. Thus the visible (> 4000 Å radiation) is responsible for much of the photolysis. We therefore propose that AIB is photolytically cleaved mostly through conversion to cis-AIB. At low temperature cis-AIB is photolyzed to nitrogen and a pair of caged t-butyl radicals which interact more often than they diffuse apart. The poor yield of $t\text{-}BuO_2\cdot$ radicals from AIB despite high concentrations of oxygen, is thus accounted for.

The thermal decomposition of cis-AIB has an activation energy of 19 kcal/mole for production of nitrogen. Trans-AIB requires 43 kcal/mole for the same process.[31] The difference of 24 kcal/mole probably reflects the large amount of steric strain associated with the cis configuration of two t-butyl groups. Another manifestation of this strain is found in the large UV shift from 3600 to 4400 Å.

At 235°K most cis-AIB isomerizes to the trans isomer with little fragmentation to N_2 and t-Bu· radicals; considerably more fragmentation occurs at 248°K (Fig. 11), indicating that isomerization and fragmentation may have a common intermediate in the caged pair of t-BuN_2· and t-Bu· radicals. Increasing temperature will lead to faster diffusion of either radical from the cage and to more extensive decomposition of t-BuN_2· radical to N_2 and t-Bu· radical.* Thermal isomerization not involving radical pairs is also possible. Isomerization due to recombination of the caged pair* can be demonstrated experimentally by an increasing proportion of isomerization with increasing solvent viscosity.

Irradiation of azoisopropane (AIP) alone or in the presence of oxygen also produces a new product with the α-hydrogen in AIP shifted 0.47 ppm downfield from the α-hydrogen in AIP. The methyl doublet of this product is shifted downfield by 0.055 ppm to overlap with the methyl doublet in AIP. We believe this product is the cis isomer of AIP.** Cis-AIP is stable at 298°K in contrast to cis-AIB which decomposes at 253°K in a few minutes, probably because of a much lower degree of steric strain present in cis-AIP.

E. Thermochemistry and Kinetics

In several experiments described in this report we have used ethane as solvent for photolysis of AIB in the presence of oxygen at 143-173°K. Under conditions of these experiments, no solvent-radical or solvent-oxygen interactions were found nor are they expected on the basis of thermochemistry and kinetics. However, the often violent reactions of frozen hydrocarbons with liquid oxygen suggest the possibility of a different mechanism for oxidation. These marked differences in behavior may become more explicable if we first consider the way thermochemistry and rates are coupled together in the system.

---

*The stability of RN_2· is undoubtedly low; however, Pryor[32] has shown from kinetic studies that at 60°C (333°K) cage recombination of $C_6H_5N_2$· + $(C_6H_5)_3C$· is significant.

**A similar photoisomerization of azomethane is reported by Hutton and Steel.[33]

1. Thermochemistry

Heats of reaction of radical-radical and radical-molecule reactions can be estimated by taking the difference in bond strengths between bonds being made and broken. For example, the reaction

$$A\cdot + BH \rightarrow AH + B\cdot$$

has a heat of reaction ΔH° equal to the bond strength D° of B-H (D°(B-H)) minus the bond strength of A-H;

$$\Delta H^\circ = D^\circ(BH) - D^\circ(AH)$$

Values of bond strengths are estimated from three papers by Benson,[34-36] and calculated heats of reaction are indicated by - for exothermic, or + for endothermic. Thermochemical calculations serve to indicate not only the ease or difficulty with which such reactions will proceed if a kinetic pathway is available, but also the quantity of heat liberated or adsorbed for a particular rate step.

2. Kinetics

Absolute values of rate constants for radical reactions are not generally available; however, it is possible to make some useful generalizations from those that have been measured.[27, 35, 36] In doing so it is convenient to discuss the rate parameters of A factor and activation energy E_a rather than specific rate constants. They are related by the equation

$$k = 10^{n-E_a/\theta}$$

where 10^n = A factor, $\theta = 2.3RT$ in kcal/mole.

Radical-radical reactions generally are very fast with A factors of 10^{10} sec^{-1} for both carbon[27] and oxy radicals.[36] Activation energies for these reactions are about 2-3 kcal in the liquid phase with the exception of some peroxy-radical interactions which may be as high as 6-10 kcal/mole.[37, 38]

Radical-molecule reactions involving transfer of H atoms from one polyatomic radical to another have A factors around 10^8 and activation energies of 8-10 kcal. Molecule-molecule reactions have A factors near 10^8 with high activation energies.

Using the thermochemical and kinetic parameters outlined, estimates can be made for rates and heats of reactions important in the low-temperature work described in this report. Table X lists the reactions that might be considered for the system:

$$t\text{-Bu}\cdot + O_2 + C_2H_6$$

Inspection of the ten reactions shows that every radical-radical reaction (including O_2) is slightly exothermic, every radical-molecule reaction is slightly endothermic, and every molecule-molecule reaction is highly endothermic. Rate constants parallel the thermochemistry.

3. Rates of Reactions at 173°K

With the kinetic parameters of Table X we can now calculate the absolute rates for selected radical and molecular processes at any temperature of interest. In this case, the experimental working temperature of 173°K is chosen to provide some examples.

A rough calculation of the heat produced by radical-radical reactions can be made using a value of 10^{18} radicals/gram as the concentration of radicals produced on impact. This is much higher than values observed in this laboratory during mechanical shearing experiments. Converting this to radicals/mole concentration and using a value of 28 kcal/mole* for conversion of carbon to peroxy radicals (reaction 3) gives

$$Q = 1.6 \times 10^{-6} \text{ mole} \times 28 \times 10^{3} \text{ cal/mole} =$$

$$45 \times 10^{-3} \text{ cal}$$

*Heats of reaction are temperature-dependent and the values quoted are at 298°K. These values may be somewhat higher at low temperatures.

TABLE X

HEATS AND RATES OF REACTION FOR THE SYSTEM

$t\text{-Bu}\cdot + O_2 + C_2H_6$

Reaction No.	Reaction	Heat of[a] Reaction, ΔH° kcal/mole	Rate Parameters[b] $\log k = A - E_a/\Theta$	
			A liter/mole/sec	E_a kcal/mole
21	$t\text{-Bu}\cdot + C_2H_6 \rightarrow i\text{-}C_4H_{10} + C_2H_5\cdot$	+8	8.5	20 ± 3
22	$t\text{-BuO}_2\cdot + C_2H_6 \rightarrow t\text{-BuO}_2H + C_2H_5\cdot$	+8	7	20 ± 3
3	$t\text{-Bu}\cdot + O_2 \rightarrow t\text{-BuO}_2\cdot$	-28	8	2 ± 1
11	$t\text{-BuO}_2\cdot + t\text{-Bu}\cdot \rightarrow t\text{-BuO}_2H + i\text{-}C_4H_8$	-51	9	2 ± 1
9	$2t\text{-BuO}_2\cdot \rightarrow 2t\text{-BuO}\cdot + O_2$	-2 ± 10	9	6 ± 1
23	$2t\text{-BuO}_2\cdot \rightarrow t\text{-Bu}_2O_2 + O_2$	-39 ± 10	8	9 ± 2
4	$2t\text{-Bu}\cdot \rightarrow i\text{-}C_4H_{10} + i\text{-}C_4H_8$	-51	10	2 ± 1
24	$C_2H_6 + O_2 \rightarrow C_2H_5\cdot + HO_2\cdot$	+51	8	65 ± 6
25	$C_2H_6 + O_2 \rightarrow C_2H_5O\cdot + HO\cdot$	+19	5	30 ± 4
26	$C_2H_6 \rightarrow C_2H_5\cdot + H\cdot$	+98	14	98 ± 1

[a] Heat of reaction is endothermic (+) or exothermic (-).

[b] Where $\Theta = 2.3RT$ in kcal/mole.

An additional 80 kcal/mole is evolved from the recombination of primary or secondary peroxy radicals which gives

$$Q = 0.8 \times 10^{-6} \times 80 \times 10^{3} \text{ cal/mole} = 64 \times 10^{-3}$$

The sum of these heats, 0.109 cal, can only produce a temperature rise of $\lesssim 1°$ if distributed uniformly through the 1 gram of hydrocarbon.** If heat distribution is restricted to the immediately surrounding molecules, much higher temperatures can be attained by factors of perhaps ten or hundred, but it is not at all clear whether such a "molecular hot-spot" can be realized.

First we can compare the relative rates of reaction of radicals with each other and with solvent ethane at 173° K. To do this requires knowledge of the concentration of radicals in the system, given by initiation and termination rates (equation numbers refer to Table I):

$$\text{AIB} \xrightarrow{h\nu} 2\text{t-Bu}\cdot + N_2 \qquad \text{initiation} \qquad \text{(i)}$$

$$\text{t-Bu}\cdot + O_2 \rightarrow \text{t-BuO}_2\cdot \qquad \text{(3)}$$

$$\text{t-Bu}\cdot + C_2H_6 \rightarrow \text{i-}C_4H_{10} + C_2H_5\cdot \qquad \text{(21)}$$

$$\text{t-BuO}_2\cdot + C_2H_6 \rightarrow \text{t-BuO}_2\text{H} + C_2H_5\cdot \qquad \text{(22)}$$

$$\left.\begin{array}{l} 2\text{t-Bu}\cdot \rightarrow \text{i-}C_4H_{10} + \text{i-}C_4H_8 \\ 2\text{t-BuO}_2\cdot \rightarrow \text{t-Bu}_2O_2 + O_2 \end{array}\right\} \text{termination} \qquad \begin{array}{l}\text{(4)} \\ \text{(23)}\end{array}$$

Equations are greatly simplified if one assumes that all radicals are either t-Bu· or $\text{t-BuO}_2\cdot$ but not mixtures, since only one kind of termination reaction need then be considered.

For the case of t-Bu· in the absence of oxygen:

Rate of initiation (R_i) = rate of termination

$$\varphi k_i(\text{AIB}) = 2k_4[\text{t-Bu}\cdot]^2, \qquad \varphi = \text{Quantum efficiency} \qquad \text{(A)}$$

$$[\text{t-Bu}\cdot] = (\varphi k_i[\text{AIB}]/2k_4)^{\frac{1}{2}} = (R_i/2k_4)^{\frac{1}{2}} \qquad \text{(B)}$$

**Specific heat may be 3-4 times smaller at 77° K than at 298° K.

The competition between termination (4) and abstraction (21)

$$\frac{4}{21} = \frac{k_4 (t\text{-}Bu\cdot)^2}{k_{21} (t\text{-}Bu)(C_2H_6)} = \frac{k_4 (t\text{-}Bu\cdot)}{k_{21} (C_2H_6)} \qquad (C)$$

from (B) and Table X is

$$\frac{4}{21} = \frac{(10^{10-3/\theta})^{\frac{1}{2}} R_i^{\frac{1}{2}}}{33 \times 10^{(8.5-18/\theta)}} \qquad \theta = 2.3R\ (173^{\circ}K) \qquad (D)$$

R_i can be set equal to the rate of disappearance of AIB in experiment 96 (at 164°K) in Table IV.

$$R_i = \frac{2(373) \times 10^{-6} \text{ mole}}{0.006 \text{ liter}} \times \frac{1}{17 \times 3600 \text{ sec}} = 2.03 \times 10^{-6} \text{ mole/liter/sec} \quad (E)$$

This rate is based on the assumption that photolysis occurs uniformly throughout the solution. It could be 100 times as large if all light is absorbed near the cell window.

Inserting the value from (E) into (D) and calculating the values for k_4 and k_{21}

$$\frac{4}{21} = \frac{(10^{3.1})(14 \cdot 10^{-3})}{2 \times 10^{-14} \times 33} \simeq 1.8 \times 10^{-14}$$

Essentially no attack by t-Bu· on ethane occurs at this temperature. The same result is obtained for the attack by t-BuO_2· on ethane (e.g., reaction 22).

Competition between reactions 3 (oxygenation) and 4 (recombination) can be calculated in the same way assuming the $[O_2] = 0.01$ mole/liter:

$$k_3 (Bu\cdot)(O_2) = k_4 (t\text{-}Bu\cdot)^2$$

$$\frac{k_3}{k_4} = \frac{(t\text{-}Bu\cdot)}{(O_2)} = \frac{10^{8-2/\theta}}{10^{10-2/\theta}}$$

$$10^{-2} = \frac{(t\text{-Bu})}{(0.01)}, \quad t\text{-Bu} = 10^{-4} \text{ mole/liter}$$

This result shows that only at rather high concentrations of t-Bu· does recombination become competitive with oxygenation, a surprising conclusion since we have encountered considerable difficulty in oxygenating all t-Bu· radicals where the [t-Bu·] must be less than 10^{-6} moles/liter.

The foregoing calculations show that at low temperature radical-radical reactions are the only ones of consequence, attack on molecules being many orders of magnitude slower. In the presence of oxygen all carbon radicals should be converted to peroxy radicals more rapidly than they can recombine with each other. That this is not observed experimentally suggests the presence of special effects such as cage restriction on radical mobility.

4. Fast Molecule-Radical Reactions

It is of interest to calculate the temperature at which the peroxy radical-ethane reaction will become competitive with radical-radical reactions, leading to chain reactions and ultimately to combustion.

For the condition that the rate of reaction 21 be equal to the rate of 22

$$R_{22} = R_{23}$$

$$k_{22}(t\text{-BuO}_2\cdot)(C_2H_6) = k_{23}(t\text{-BuO}_2\cdot)^2$$

$$k_{22}/k_{23} = (t\text{-BuO}_2\cdot)/(C_2H_6)$$

$$\frac{k_{22}}{k_{23}} = \frac{10^7 10^{-18/\theta}}{10^8 10^{-8.6/\theta}} = \frac{10^{-6}}{30}$$

$$10^{-1}\ 10^{-9.4/\theta} = 3 \times 10^{-8}$$

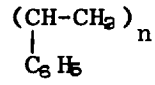
$$10^{-9.4/\theta} = 3 \times 10^{-7}$$

$$\theta = \frac{9.4}{6.52} = 1.44$$

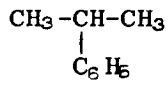
$$T = 314^{\circ}K \text{ or } 41^{\circ}C$$

This calculation gives a minimum value for T, since our estimate of 18 kcal for E_a is probably a minimum value for the abstraction step. For an activation energy of 23 kcal, $T \cong 470^\circ K$ or $200^\circ C$.

If the same kind of calculation is carried out for peroxy radical abstraction on polystyrene, which has a structural unit similar to that for cumene, we can use the rate parameters for cumene oxidation.



polystyrene



cumene

The ratio of rate parameters for propagation to rate parameters for termination has been measured in this laboratory.

$$C_6H_5CHMe_2 + RO_2\cdot \rightarrow C_6H_5\dot{C}Me_2 + RO_2H \qquad (27)$$

$$k_{27}/k_{23} = 10^{-1.8}\ 10^{-4.2/\theta}$$

$$k_{27}/k_{23} = (RO_2\cdot)/(C_6H_5CHCH_2)_n$$

$$\log k_{27}/k_{23} = \log\left[(10^{-6})/(10)\right] = -1.8 - (4.2/\theta)$$

$$-7 + 1.8 = -4.2/\theta$$

$$\theta = -5.2/4.2 = 1.24$$

$$T = 270^\circ K \text{ or } -3^\circ C$$

5. Chain Branching Processes

Although our calculations show that chain processes are possible at moderate temperatures, this first chain step, formation of hydroperoxide and a new alkyl radical which is quickly oxygenated, gives a net heat for the cycle of only +33 to -8 kcal/mole. Formation of hydroperoxide is about 30 kcal/mole exothermic, or about 8% of the heat of combustion of ethane.[39]

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O, \qquad \Delta H^\circ = -368 \text{ kcal/mole}$$

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot, \qquad \Delta H^\circ = -5 \text{ to } +20$$

$$R\cdot + O_2 \rightarrow RO_2\cdot, \qquad \Delta H^\circ = -28 \text{ kcal/mole}$$

A comparable reaction at high temperature to form olefin and H_2O_2 is almost thermoneutral.

Thus, most of the heat of combustion of organic compounds is released at later stages in the oxidation by reactions that are normally observed at higher temperatures, i.e., > 200°C or 473°K. In order for slow oxidation to accelerate to combustion temperatures, additional chemical steps are needed that produce a multiple of the starting radicals. In oxidation these chain branching steps are thought to be the result of hydroperoxides or hydrogen peroxide.

$$ROOH \rightarrow RO\cdot + HO\cdot, \qquad \Delta H^\circ = +43 \text{ kcal/mole}$$

$$RH + HO\cdot \rightarrow R\cdot + H_2O, \qquad \Delta H^\circ = -20\text{-}35 \text{ kcal/mole}$$

$$RH + RO\cdot \rightarrow R\cdot + ROH, \qquad \Delta H^\circ = -(4\text{-}17) \text{ kcal/mole}$$

$$2R\cdot + 2O_2 \rightarrow 2RO_2\cdot, \qquad \Delta H^\circ = -56 \text{ kcal/mole}$$

This cycle is at least 37 kcal and possibly 65 kcal exothermic. The only other obvious exothermic reactions are radical-radical recombinations (Table X, reactions 3 and 9). However, these reactions stop chains, and if new chains are to be generated, very slow endothermic molecule-molecule reactions are required (Table X, reactions 24-26). The deflagrative reactions observed with organic compounds and liquid oxygen thus involve many kinetic rate steps over a wide temperature range.

Detailed understanding of the initiation process necessarily requires an explanation of how, once started, the liquid oxygen-organic system is able to sustain exothermic chemical reactions.

Our work has demonstrated that radicals can be produced under impact-like conditions; however, these radicals do not subsequently start fires on introduction of liquid oxygen. This implies that whatever radical-radical reactions may ensue, the exothermicity is insufficient to produce

any localized chain temperature and that instantaneous localized heating must accompany radical formation in order for a chain temperature to be attained.

IV CHARACTERIZATION OF FLUOROSILICONE GREASE SAMPLES

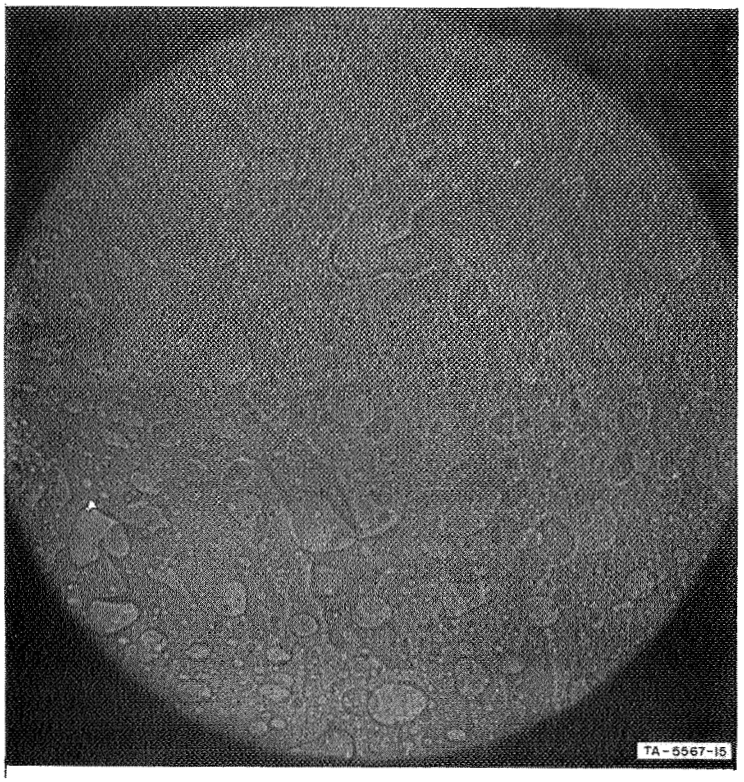
Two samples of fluorosilicone greases (SM-S and SM-U) were sent to us by NASA-Huntsville to establish, if possible, the physical or chemical differences between the samples that are responsible for one grease (SM-U) being unacceptably sensitive to impact when frozen in liquid oxygen while the other (SM-S) is not. Both greases were presumably prepared in the same way from a fluorosilicone fluid thickened with 100-200 Å diameter silica particles.

Infrared and nmr spectra of both samples failed to reveal significant chemical differences between them, a finding consistent with the claim that the same sample of fluid was used for both batches. Physical properties of the samples are clearly different. One grease (SM-U) is thick and very viscous; the other (SM-S) is much more fluid.

Studies by optical microscopy indicate that the sample designated SM-S consists of a fluid thickened with unresolvable submicron particles of silica filler that form a matrix in which may large globules of fluid are suspended. The globules range in size from 5 to 100 microns in diameter and occupy an estimated 20-30% of the grease volume. These are the large spherical objects seen in Fig. 2 of Quarterly Progress Report No. V.[8] Sample SM-U is also a suspension of unresolvable particles; only about 1 volume percent of this grease is fluid globules, and their size is fairly uniform--10-20 microns in diameter. These differences are clearly seen in the photomicrographs at 200 magnifications in Figs. 12a and b.

The particles of silica filler are much too small to be seen by optical microscopy. To determine whether the size of the silica particles was similar in the two greases, fluid-free samples of both silica fillers were prepared for electron microscopy studies. Thin films of each grease were placed on a Nichrome ribbon heated to 230-240°C (503-513°K) at

*The microscopy studies described here were carried out by Dr. Saul Chaikin of the Inorganic and Physical Chemistry Department.



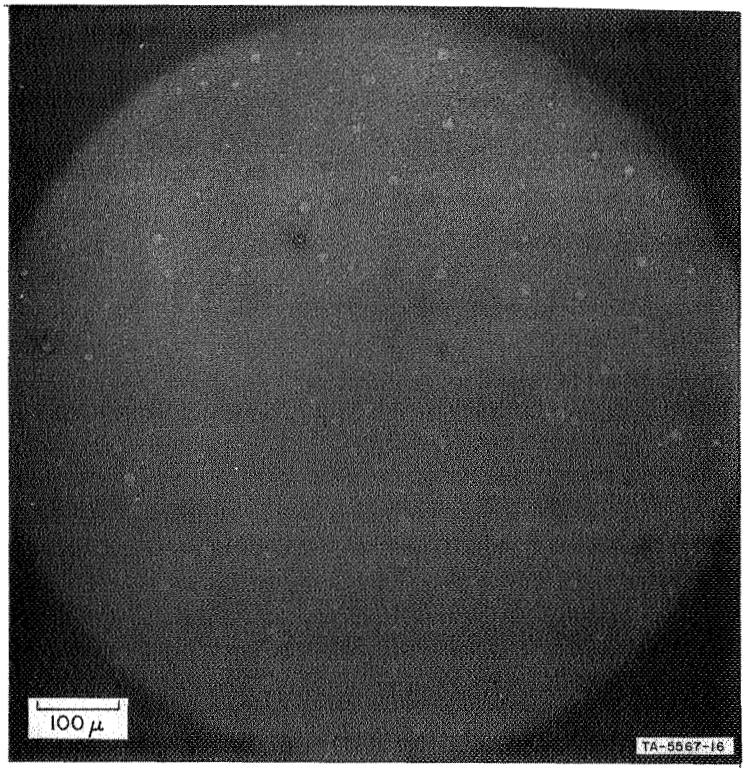


FIG. 12 PHOTOMICROGRAPHS OF FLUOROSILICONE GREASE

10^{-4} torr. After two hours SM-U gave a clear photomicrograph at 80,000 magnifications (Fig. 13). SM-S could not be entirely freed of fluid even on heating for $2\frac{1}{2}$ hours at a somewhat higher, but unknown, temperature. Figure 14 shows that the dispersion still contains appreciable amounts of opaque fluid. However, particle sizes in both samples are very similar (between 100 and 200 Å), indicating the same thickener was used in each case.

The difficulty experienced in removing fluid from one sample may be the result of a higher molecular weight range for that particular sample of fluid. Experiments now in progress are directed toward measuring the molecular weight range of each fluid and the properties of fluid in each sample.

Attempts to separate large samples of fluorosilicone fluid from the grease using a molecular still heated to 235°C (508°K) at 10^{-4} torr failed to effect any separation. Alternative methods of separation such as filtration, centrifugation, or adsorption will be sought.

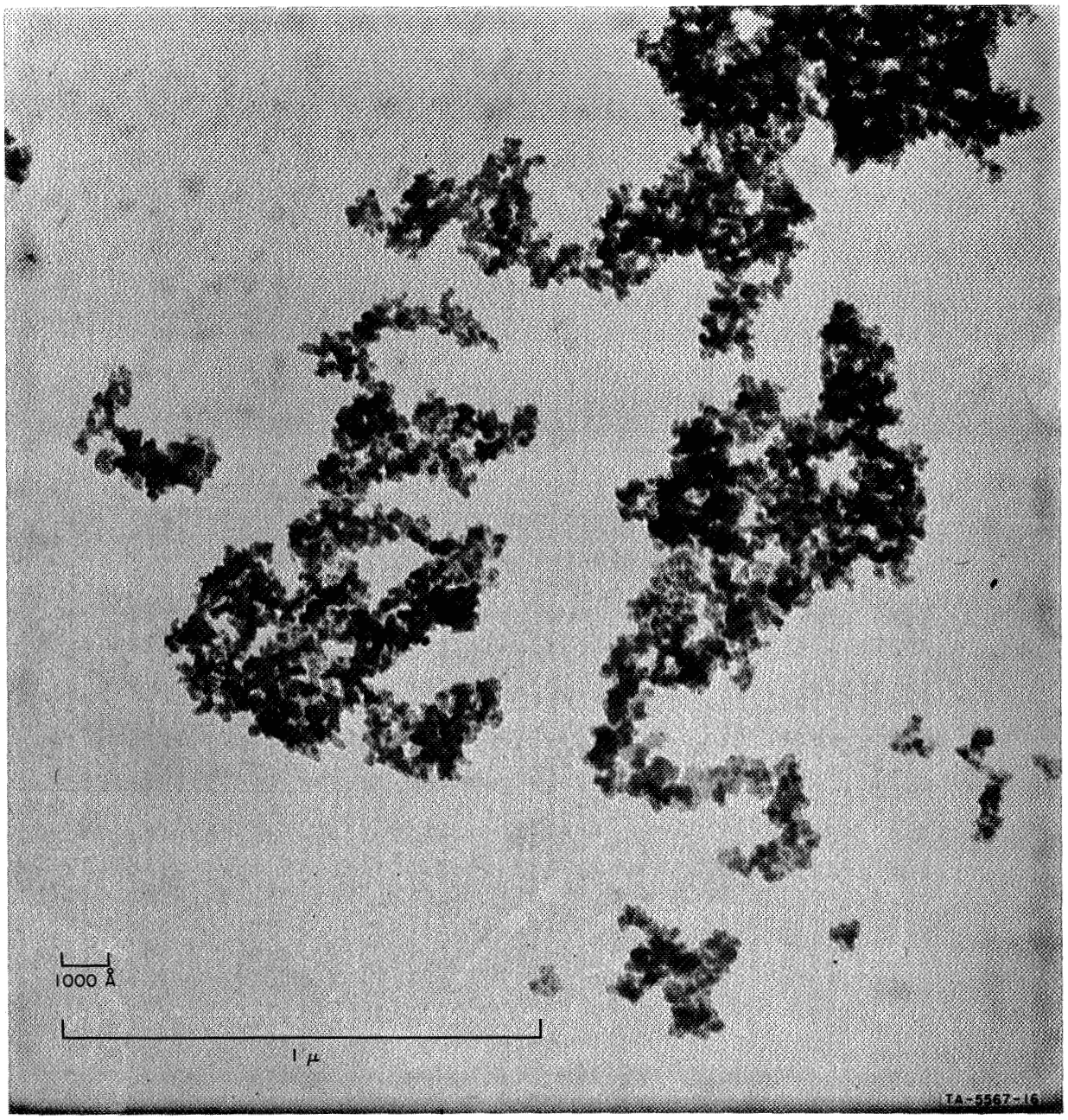


FIG. 13 ELECTRON PHOTOMICROGRAPH OF SILICA FILLER FROM UNAPPROVED FLUOROSILICONE GREASE

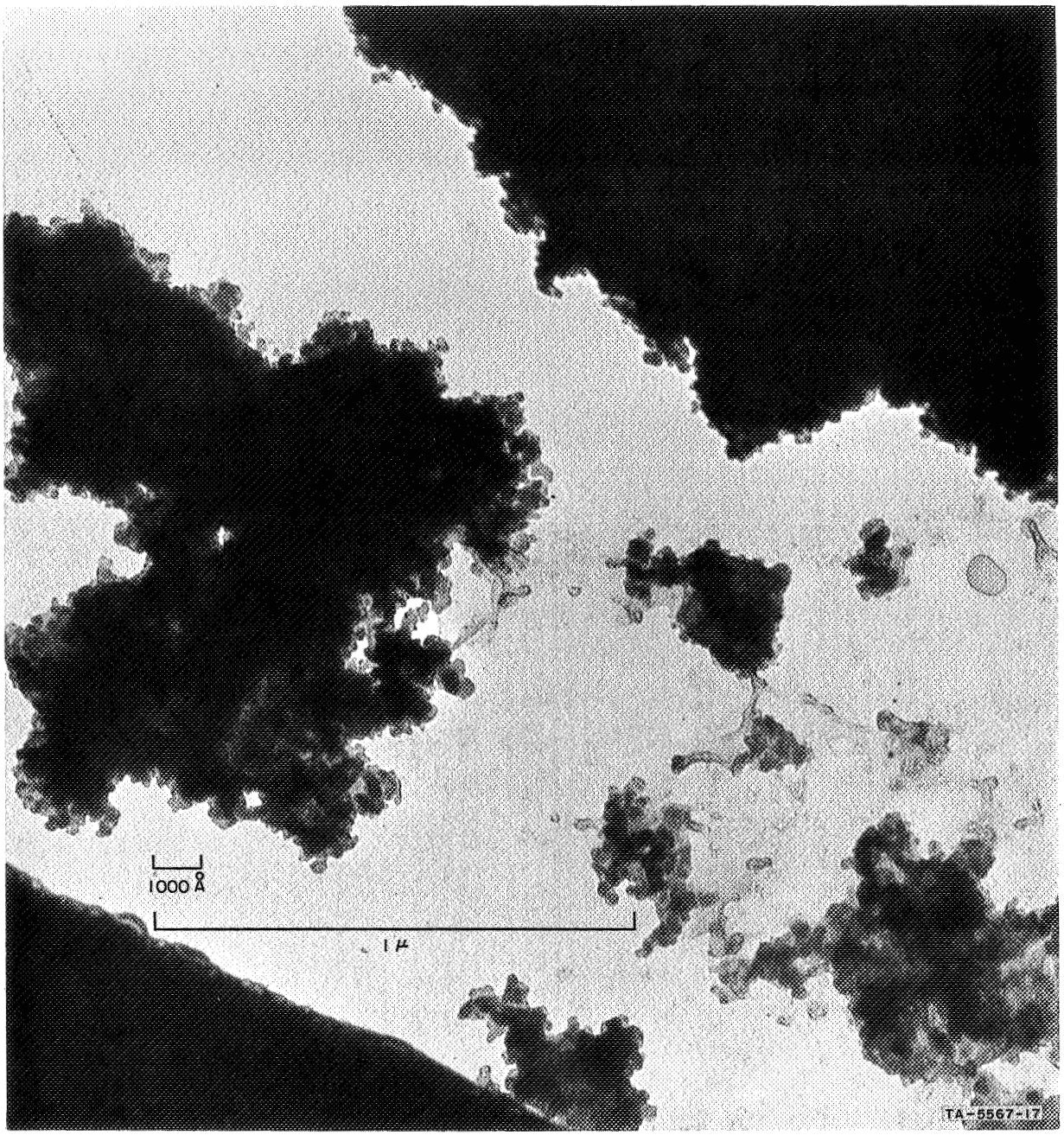


FIG. 14 ELECTRON PHOTOMICROGRAPH OF SILICA FILLER FROM APPROVED FLUOROSILICONE GREASE

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CONCLUSION

The work described in this report is concerned with two different but related aspects of the problem of impact ignition of organic compounds in the presence of liquid oxygen (LOX). The initial hypothesis was that free radicals played an important role in impact-ignition phenomena and one part of the research has been concerned with the possible generation of free radicals under impacting conditions, and the subsequent reaction of these free radicals with oxygen. Last year we were able to demonstrate that large quantities of hydrocarbon free radicals can be generated under simulated impact but that their reaction with oxygen, though rapid, was not sufficiently exothermal to cause ignition in any of the samples tested. During this second year this phase of our research has continued in the same general direction. We have been able to confirm that impact of polystyrene under the ABMA machine produces carbon radicals of the same type and in quantities comparable to those produced in the simulated process. We know now that these radicals react rapidly and spontaneously to produce peroxy radicals, but this reaction does not, alone, account for ignition.

However, the hot-spot hypothesis which explains the impact sensitivity of ordinary explosives is also applicable to this heterogeneous situation. Photographic records obtained during and subsequent to impact show that ignition does not occur simultaneously throughout all, or even a major part of the sample but, rather, originates at one or more points. Also, abrasives can increase the sensitivity of low-melting hydrocarbon polymers. We conclude from these studies that hot-spot formation is probably necessary for impact ignition. On the other hand carbon free radicals, though definitely present and reactive have, as yet, an unassigned role.

The second phase of this work has been concerned with elucidating the detailed reactions of t-butyl peroxy radical below 200°K under

various conditions and with examining the effect of structure on the reactions of alkylperoxy radicals in the low temperature regime.

From the results of this year's work we conclude the following:

1. In the absence of very reactive hydrogen donors t-butyl peroxy radicals react only with each other at 200°K to produce t-butyl tetroxide. The tetroxide decomposes above 180-200°K to give oxygen and t-butoxy radicals.

2. t-butoxy radicals can abstract hydrogen even from poor hydrogen donors at 200°K to form t-butyl alcohol. t-butoxy radicals can also interact with peroxy radicals to form di-t-butyl trioxide which is unstable above 250°K. Very little di-t-butyl peroxide is formed as compared with t-butyl alcohol even below 200°K.

3. A very reactive hydrogen donor such as HI can scavenge t-butyl peroxy radicals even at 200°K, thus preventing or minimizing tetroxide formation. The photolysis of t-butyl iodide with oxygen is complicated and different from the photolysis of AIB with oxygen because of the concomitant formation of HI in the former t-butyl iodide-oxygen system.

4. Isopropyl peroxy radical which is a secondary radical apparently forms a tetroxide which is unstable even at 140°K. Cleavage of this tetroxide gives oxygen, acetone, and isopropyl alcohol but no s-propyloxy radicals. This marked effect of structure on reactivity is undoubtedly caused by the presence of α-hydrogens in the di-s-propyl tetroxide structure which permits a direct cleavage to non-radical products.

5. Trifluoromethyl peroxy radical behaves much like isopropyl peroxy radical in that it produces no stable tetroxide or trioxide even at 140°K. In this case, however, the only reasonable pathway for decomposition to COF_2, the only primary product, involves the interaction of iodine atom and $CF_3O\cdot$. Thus the complicating feature of this system is the presence of a significant steady-state concentration of iodine atoms. In the absence of iodine, trifluoromethyl peroxy radicals might give entirely different products.

6. Thermochemical and kinetic estimates of reactivity of simple organic compounds indicate that exothermic propagation steps involving peroxy radicals cannot be important below 300°K, and they probably do not become really significant in many organic systems until the temperature exceeds 350-400°K. Although alkoxy radicals are much more reactive than peroxy radicals, they are not generated from secondary peroxy radicals at low temperatures. Experimental data cited above support this conclusion.

We now consider how these experimental results apply to the problem of impact sensitivity of organic compounds at LOX temperatures. Although free radicals may be generated in significant numbers by impacting at low temperatures it is now clear that these radicals will not propagate exothermic oxidation chain reactions at these temperatures; instead the radicals will disappear by mutual interaction. Only if the temperature is high enough will propagation exceed termination and lead, through successive intermediate steps, to the very fast, very exothermic combustion regime. Thus during the very short time interval from initial impact to detectable deflagration, the temperature of the system must rise many hundreds of degrees and the great bulk of oxidation reactions takes place above 300-400°K. This is consistant with the conclusion that hot spots are a necessary feature of the impact sensitivity phenomenon. If this interpretation is correct, there will be little gained by extending our present low temperature studies of peroxy radicals to still lower temperatures; instead we need to examine the effect of increasing temperature on the ratio of propagation to termination and the effect of molecular structure on this ratio. An examination of the oxidation of selected groups of simple organic compounds at temperatures above 300°K is one way to do this and it may provide some insight into the reactivity patterns observed from impact tests. Further, the use of a chemical probe such as t-butoxy radical to measure reactivity of C-H bonds in organic compounds might also provide in a very simple way the structure reactivity relationships needed for selecting LOX-compatible organic compounds.

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